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AN ASSESSMENT OF THE SULFURIC ACID AEROSOLS, HYDROCARBONS AND RESPIRABLE COMBUSTIBLE DUST IN THE UNDERGROUND MINE ENVIRONMENT

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Lorraine A. Baldisera

and

Kenneth C. Westaway

Chemistry Department

Laurentian University

Subdury, Ontario

P3E 2C6

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ABSTRACT

Four different types of filters for collecting sulfuric acid mist samples and respirable combustible dust (RCD) samples in dieselized underground mines have been assessed. The silver membrane filter has been judged superior for collecting both the sulfate ion and the RCD samples.

A combination of sulfate ion, pH and RCD analyses on the silver membrane filters and sulfate ion analyses of "MasKery Badges" developed by Mr. David MasKery of Inco Metals Co. in Sudbury, have enabled us to determine the amounts of sulfate ion, sulfuric acid, sulfur dioxide, carbon, water and both the respirable and respiriable combustible dust (the RCD) in many different mining environments in four nickel mines. The results show that the average sulfate ion concentration is only half of the TLV value for sulfuric acid and that very little of the sulfate ion is present as sulfuric acid at the sampling site. This study also shows that very little of the sulfur compounds in the fuel can be detected (are recovered) in the mine environment. The results suggest that the sulfuric acid dissolves in water droplets that settle out of the mine air very rapidly.

Several laboratory studies have suggested that the catalytic purifiers used on diesel engines generate a sulfuric acid mist that is released into the mine environment. Our results suggest that the amount of sulfuric acid in the mine environment is far below the TLV level in nickel mines whether the diesel is fitted with a catalytic purifier, a fume diluter, a Corning diesel exhaust filter or has no exhaust treatment device.

Ammonia analyses show that the (ammonia/sulfate ion) ratio can be as large as 1.0 near a mucking site. The presence of ammonia further reduces any concern about sulfuric acid aerosols in the mine environment because ammonia can neutralize any sulfuric acid that is present in the mine air. All of these facts make it unlikely that miners are exposed to significant levels of sulfuric acid mist in nickel mines.

Finally, it appears that the sulfuric acid levels in the mine air are related ot the amount of sulfur in the fuel. It would be wise therefore, to continue to use low sulfur fuels in underground mines.

Considerable time has also been spent determining the composition of the respirable combustible dust (RCD) samples collected in underground mines. This work has shown that the approximate composition of the RCD sample is 0.1% PAHs (polynuclear aromatic hydrocarbons),

25% hydrocarbon and/or carbon particles (diesel soot) and 2% sulfuric acid. Thus, only 30% of the respirable combustible dust has been identified.

The analyses of the RCD samples collected in the local mines has shown that the average RCD levels are only 30% of the generally accepted level of 2 mg/m^3. Finally, the RCD only accounts for 55% of the respirable dust collected on the silver membrane filter. This means that a significant portion of the respirable dust sample is respirable-sized particles of ore.

Our investigation of the RCD showed there was more sulfate ion on the silver membrane filters after they had been heated in the RCD experiment. This confirmed the results of the sulfate ion-pH analyses, ie., that almost all of the sulfate ion on the filters was present as sulfate ion and not sulfuric acid.

Adding a catalytic purifier to the exhaust system of the diesel reduces the amount of carbon and almost doubles the percent (sulfate ion/RCD). Surprisingly, the catalyst does not increase the percent (sulfuric acid found/sulfuric acid expected if all of the sulfate ion were present as sulfuric acid) or the percent (sulfuric acid/RCD) significantly.

Adding a fume diluter increses the amount of sulfate ion in the RCD sample slightly but does not affect the percent (sulfuric acid found/sulfuric acid expected if all of the sulfate ion were present as sulfuric acid) or the percent (sulfuric acid/RCD) significantly.

When the Corning diesel exhaust filter was added to the diesel, the percent (carbon/RCD) and the percent (RCD/Total respirable dust) were reduced. The surprising result was that the percentage of both the (sulfuric acid/RCD)and the precent (sulfate ion/RCD) were much higher when the Corning filter was used. The percent (sulfuric acid/sulfuric acid expected if all of the sulfate ion were present as sulfuric acid) does not change when the Corning filter is added to the exhaust system of the diesel. This suggests that the increased percentages for the (sulfate ion/RCD) and (sulfuric acid/RCD) may be the result of an error in the RCD analysis.

Finally, it appears that burning a more aromatic, higher sulfur fuel in the diesel increases the RCD, decreases the percent carbon and increases the amount of sulfate ion and sulfuric acid in the exhaust.

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INTRODUCTION

Several years ago, catalytic purifiers were added to the exhaust train of the diesels used in underground mines to reduce the concentrations of some of the pollutants that are generated when diesel fuel is burned in the engine. Although the catalysts are effective in lowering the concentrations of carbon monoxide (CO) and unburned hydrocarbons in the exhaust, they do so at a price. Several workers (1,2) have indicated that the catalysts also oxidize the sulfur dioxide (SO_2) that is formed when the sulfur compounds in the fuel are burned in the engine, to sulfur trioxide (SO_3). This is of concern because the sulfur trioxide would react instantaneously with the water in the hot exhaust to form sulfuric acid, equation 1.

$$\text{Fuel S} \longrightarrow SO_2 \xrightarrow{\text{catalyst}} SO_3 \xrightarrow{H_2O} H_2SO_4 \qquad [1]$$

Presumably, the sulfuric acid leaves the diesel as a vapour. The acid molecules would either condense to form a fine mist (aerosol) or be adsorbed on the respirable-sized (soot) particles (3) that are formed when the fuel is burned in the combustion chamber of the diesel.

The conversion of sulfur dioxide to a fine sulfuric acid mist or aerosol is of concern to those working around or downstream from a diesel because the TLV for sulfuric acid mist is very low, ie., 1 ppm. (4). The TLV is low because the corrosive sulfuric acid could be inhaled as an aerosol or on the respirable-sized soot particles, and be deposited on the surface of the lung where it could destroy the lung tissue.

Two different studies by Kirk and co-workers (5,6) suggested that there was some reason for concern. These workers attempted to determine the concentration of the sulfuric acid in the air of a uranium mine by collecting both respirable and total dust samples on glass fiber filters and analyzing the filter extracts for sulfate ion. In fact, Kirk et. al. found sulfate ion concentrations as high as 2 mg/m^3 in the mine air. Thus, if all of the sulfate ion were present as sulfuric acid, the TLV for sulfuric acid would have been exceeded by a factor of two. In addition, Kirk's work showed that most, if not all (80% ± 26%) of the sulfate ion (sulfuric acid) was associated with the respirable-sized particulate. This meant that the acid could be drawn into a miner's lung where it could cause a health problem.

Our initial study (7) was undertaken in an effort to determine the magnitude of the sulfuric acid mist problem in other mines and to assess whether the current generation of catalytic purifiers improved or worsened the mine environment from this point of view. In this study,

a new (spectroscopic) method was developed for analyzing the sulfate ion in both the total and the respirable dust samples collected on Gelman teflon-coated glass fibre and on Whatman GF/A glass fibre filters. Although the results from the samples collected in a nickel mine (7) were in general agreement with those reported by Kirk et. al., there were small differences in the results from the two mines. First, although the sulfate ion concentrations in the nickel mines were generally lower than those found in the uranium mine, the results from the nickel mine samples indicated that the sulfuric acid levels could be at or above the TLV value for sulfuric acid if 1) the ventilation was at the required level of 100 cfm/brake horsepower and 2) if all of the sulfate ion was present as sulfuric acid. Secondly, all (100%) of the sulfate ion was associated with the respirable dust fraction of the particulate in the nickel mine samples whereas only 80% $\pm$ 26% of the sulfate ion was with the respirable dust component of the samples collected in the uranium mine. Another small difference between the results obtained in the nickel and uranium mines was the relationship between the sulfate ion and the amount of respirable combustible dust. When Kirk and co-workers assumed that all of the sulfate ion in the mine air was present as sulfuric acid and that this acid was lost when the filter was heated in an RCD experiment, they found that the sulfuric acid accounted for 53% of the total weight loss in the RCD experiment. When the same calculations were carried out on the samples collected in the nickel mines, the sulfuric acid only accounted for 17% of the weight loss in the RCD experiment.

The one surprising aspect of the results from the nickel mine samples was that the extracts from the respirable and total dust samples were not as acidic as had been expected. In fact, a pH analysis of the filter extracts ranged from very slightly acidic to basic, ie., the pH varied from 6.4 to 7.2 with an average pH of 6.84. If all of the sulfate ion had been present as sulfuric acid, the pH of the filter extracts would have been between 3.2 and 4.6 with an average pH of 3.83. In fact, a comparison of the expected and the actual pH of the filter extracts suggested that only 0.1% of the sulfate ion on the filters was present as sulfuric acid. This was surprising because oxidation of the SO_2 in the exhaust system would undoubtedly yield sulfuric acid. Although some suggestions for the low acidity were presented, the lack of acidity in the filter extracts remained unexplained.

This study was undertaken in an effort to 1) confirm the results of our initial study of the concentrations of the sulfuric acid mist in the mine air, 2) to determine whether the sulfate ion was present as sulfuric acid or as a sulfate salt and 3) to attempt to determine the composition of the RCD samples collected in dieselized underground mines.

RESULTS AND DISCUSSION

SELECTION OF THE FILTER

The first requirement was to ensure that the filters used to collect the sulfate ion and respirable combustible dust samples in the mine did not introduce any errors in the analysis. The most important aspect of this study involved examining the filters used in collecting the sulfate ion samples to ensure that the high pH of the filter extracts was not the result of a sampling artifact. This was important because the pH analysis in the initial study indicated that very little of the sulfate ion was present as sulfuric acid even though 1) sulfuric acid is the only substance that could have been formed when the sulfur dioxide was oxidized in the catalyst and 2) other workers had reported large increases in sulfuric acid when oxidizing type catalysts were installed on the diesels used in underground mines (1,2).

Currently, four different types of filters,

1. the Whatman GF/A filter used in our initial study,
2. a silver membrane filter,
3. a polyvinylchloride (PVC) filter and
4. a cellulose filter,

are being used in mine air monitoring. Each of these filters were assessed from four different points of view; 1) the pH of the blank filter extracts, 2) the buffering capacity of the filter, 3) the amount of extractable sulfate ion in the filters, ie., the sulfate ion blank and 4) the amount of sulfate ion produced when a known quantity of SO_2 was drawn through the filter. The results of these control experiments are given in Table 1.

1. The pH of the filters:- The pH of the four different filters was determined by measuring the pH of the solution that was obtained when each filter was extracted (stirred) with 10 ml of deionized double-distilled water for 10 min. The results in Table 1 show that the pH of the filter extracts are quite different. Our initial premise (7) was that the Whatman filter should be used because the filter extract was neutral, ie., had a pH of 7.00. This idea was wrong however, because the water used in the analysis contained dissolved carbon dioxide and

Table 1 Filter testing for pH, buffer capacity, blank size and the oxidation of sulfur dioxide.

Test	Whatman GF/A Filter	Silver membrane Filter	Polyvinylchloride Filter	Cellulose Filter	Water
pH of the filter extract	7.09 6.97 7.06	5.82 5.44 5.51	6.20 5.55 6.18	6.35 5.89	5.41 5.59 5.42
	Ave 7.04 ± 0.06	Ave 5.59 ± 0.20	Ave 5.98 ± 0.37	Ave 6.12 ± 0.33	Ave 5.47 ± 0.10
pH of the filter extract when 0.07mg of sulfate ion was put on a filter as sulfuric acid	5.08 6.26 6.08	4.01 3.90 3.94 4.10	3.91 3.96 4.27 4.04	3.98 3.97 4.00	3.98 3.98 3.79
	Ave 5.81 ± 0.64	Ave 3.99 ± 0.09	Ave 4.05 ± 0.16	Ave 3.98 ± 0.02	Ave 3.92 ± 0.11
mg sulfate ion in the filter extract from a blank filter	0.19 0.10 0.07	0.01 0.02 0.02	0.03 0.03 0.06	0.01 0.04	
	Ave 0.12 ± 0.66	Ave 0.02 ± 0.02	Ave 0.04 ± 0.02	Ave 0.03 ± 0.02	
mg sulfate ion when 39ℓ of a 50:50 sulfur dioxide-oxygen mixture was drawn through the filter	0.18 0.21	0.01 0.02 0.00	0.07 0.07	0.04 0.04	
	Ave 0.20± 0.02	Ave 0.01± 0.01	Ave 0.07 ± 0.00	Ave 0.04 ± 0.00	

was therfore, acidic, ie., had an average pH of 5.47. Thus, if the filter extract did not add any acid or base, the pH of the filter extract should have been 5.47. Since the Whatman GF/A filter extract had a pH of 7.04, the Whatman filters consumed the acid in the water and were therefore, basic. When the results of the pH testing are viewed in this way, the most attractive filter is the one whose extract is the closest in pH to that of the deionized double-distilled water used in these tests, ie., to 5.47. Thus, the best filter is the silver membrane filter where the difference in the pH of the water and the extract is only 0.12 pH units. The second best filter is the PVC filter with a pH difference of 0.51. The cellulose and the Whatman GF/A filters with pH differences of 0.65 and 1.57, respectively, are not acceptable if one wishes to determine the amount of sulfuric acid in mine air samples.

2. The buffering capacity of the filters:- The unexpectedly high pH (low acidity) of the filter extracts led us to wonder whether some of the sulfuric acid that had been collected on the filters had been consumed (reacted with or was neutralized) by the filter. In order to eliminate this possibility, a known amount of acid was put on each filter. Then, the filter was extracted and the pH of the extract determined in the usual manner. In addition, a control experiment was done by adding the same amount of acid to 10 ml of deionized double-distilled water. The pH of the 10 ml. water sample in the control experiment was 3.92. If the filter neutralized any of the sulfuric acid, the pH of the filter extract would be higher than 3.92. The results in Table 1 show that the Whatman GF/A filters have a large buffering capacity, ie., they consume (neutralize) a significant amount of acid and raise the pH by almost two pH units. In fact, the average Whatman GF/A filter consumes approximately 1.4×10^{-6} moles of acid. If all of the sulfate ion in the mine air had been present as sulfuric acid, then approximately 22% of the sulfuric acid would have been neutralized (converted into sulfate salts) by this filter. This would obviously produce a large error in the pH analyses, ie., one would underestimate the amount of sulfuric acid in the mine air significantly. The silver membrane, the PVC and the cellulose filters on the other hand did not consume significant amounts of sulfuric acid. The cellulose and silver membrane filters are clearly the best from this point of view, ie., the difference between the observed and expected pH for these filters is only 0.06 and 0.07 pH units, respectively. Even the PVC filter with a pH difference of 0.13, is acceptable. In fact, these filters only consumed approximately 1.0×10^{-7} moles of acid (about 1% of the acid that would be on the filters if all of the sulfate ion were present as sulfuric acid).

3. The amount of sulfate ion on the filter:- All four filters were analyzed for sulfate ion using the spectrophotometric analysis developed in the initial study (7). These tests were

done to ensure that the filter did not contain significant amounts of sulfate ion. The results in Table 1 indicate that the blanks were low for all but the Whatman GF/A filters. In fact, the silver membrane filter had the lowest amount of sulfate ion. The cellulose and PVC filters also contained very small amounts of sulfate ion and were judged acceptable for this study, ie., the blanks for all three filters were the same within the experimental error of the method.

4. Oxidation of the sulfur dioxide on the filter:- Our initial study had shown that significant amounts of SO_2 was oxidized to SO_3 (H_2SO_4) on the Gelman and the Whatman GF/A type filters (7). Since the final product of the oxidation of sulfur dioxide is sulfuric acid, any oxidation would introduce an error in both the sulfate ion and the pH analyses. It was important, therefore, to test the filters from this perspective. The actual test involved determining the amount of sulfate ion on the filter after 39 litres of a 50:50 sulfur dioxide-air mixture had been drawn through the filter at a rate of approximately 2 litres/min; the rate used in collecting most of the sulfate ion samples in the mine. The results in Table 1 show that almost no sulfate ion is formed on the silver membrane filter. In fact, only 0.01 mg of sulfate ion was detected when 39 liters of the SO_2 mixture was drawn through the silver membrane filter. Only a small amount of sulfate ion (0.04 mg) was found on the cellulose filter. The amount of oxidation was at least two times higher (0.07 mg of sulfate ion was found) on the PVC filter and was almost seven times higher (0.20 mg of sulfate ion was found) on the Whatman GF/A filter. Thus, although the Whatman filters were clearly superior to the Gelman filters examined in the inital study (7), the Whatman GF/A filters were much poorer than the other filters investigated in this study.

Conclusion:- The results from the examination of the filters indicates that the silver membrane filter is clearly the best filter for collecting the sulfate ion (sulfuric acid) samples in dieselized underground mines. In fact, the silver membrane filter was superior from all but one point of view and it was only marginally worse than the best filter in this test, ie., it was i) neutral and caused the smallest change in the pH of the water used to extract the filters, ii) it had within experimental error, the lowest buffering capacity, iii) was the lowest in extractable sulfate ion and iv) oxidized less sulfur dioxide than the other filters. The cellulose filter was eliminated because it neutralized a significant amount of sulfuric acid and would give significant errors in the pH analysis. The PVC filter was unacceptable because it oxidized too much SO_2 to sulfuric acid. The Whatman FG/A filters were judged unacceptable in all four tests. As a result, all of the sulfate ion underground samples should be collected on silver membrane filters.

AMMONIA IN THE MINE ENVIRONMENT

One suggestion for the lack of acidity in the sulfate ion samples collected in dieselized underground mines was that the sulfuric acid produced in the catalytic purifier was neutralized (converted in ammonium hydrogensulfate and/or the neutral ammonium sulfate) in a reaction with ammonia, equation 2.

$$NH_3 + H_2SO_4 \longrightarrow NH_4HSO_4 \xrightarrow{NH_3} (NH_4)_2SO_4 \qquad [2]$$

This explanation for the reduced acidity seemed plausible because some of the ammonia that can be formed when the ammonium nitrate-diesel fuel explosive is detonated in the blasting operation, can be trapped in the spaces between the rocks in the muck pile. This ammonia which would obviously be released into the mine air when the rock is moved during the mucking portion of the LHD cycle, could either react with 1) the sulfuric acid mist in the mine air to form very small (light) particles of ammonium hydrogensulfate and/or ammonium sulfate that would be collected in the respirable dust samples, or 2) the sulfuric acid on the silver membrane filter. Since forming the ammonium salts consumes sulfuric acid, the acidity of the filter extracts would be reduced and the pH would be higher.

A method for determining the ammonia in water samples (8) was modified so that we could measure the amount of ammonium ion (ammonia) in the aqueous extracts from the respirable dust samples collected in an underground mine. This allowed us to determine whether the blasting could generate enough ammonia to neutralize a significant portion of the sulfuric acid in the mine atmosphere, ie., to reduce the acidity of the filter extracts significantly.

The colourimetric analysis for ammonia was carried out on a portion of the filter extract solution that was used for the pH and sulfate ion analyses. These analyses indicated that significant amounts of ammonia can be released during the mucking operation. For example, the results in Table 2 indicate that the (ammonium ion (ammonia)/sulfate ion) ratio on the respirable dust samples collected near a mucking site in a nickel mine range from 0.18 to 1.00 with the average (ammonium ion/sulfate ion) ratio equal to 0.53 ± 0.24. This means that there is enough ammonia in the average mine air to convert approximately half of the sulfuric acid into the less acidic ammonium hydrogensulfate, equation 3.

Table 2 The ammonia and sulfate ion concentrations and the (ammonia/sulfate ion) ratios at various locations in a stope where a 78 horsepower Deutz diesel was mucking ore.

Location	Sulfate[a,b] ion mg/m^3	Ammonia[a] mg/m^3	$\left[\frac{\text{Moles ammonia}}{\text{moles sulfate ion}}\right]$[b]	pH of 10ml filter extract	Moles H^+ ion X 10^8 found	Moles H^+ ion expected from the sulfate ion X 10^6	% Sulfate ion present as Sulfuric acid
Central	2.31	0.41	1.00	5.09	8.06	17.70	0.46
Central	1.12	0.06	0.28	4.66	21.92	8.34	2.6
Central	1.23	0.13	0.58	5.39	4.08	12.08	0.34
Central	1.23	0.13	0.61	5.89	2.58	13.54	0.19
Muck Pile	1.51	0.05	0.18	6.38	0.417	12.92	0.03
Muck Pile	1.60	0.13	0.45	-	-	15.62	-
Stope Exhaust	1.70	0.15	0.49	6.16	0.692	16.66	0.04
Stope Exhaust	2.18	0.15	0.40	6.27	0.537	17.70	0.03
Stope Exhaust	3.12	0.16	0.81	5.56	2.76	7.28	0.38
Mill Hole	3.40	0.46	0.54	5.17	6.73	26.00	0.26
Averages			0.53 ± 0.24				0.48% ± 0.81%

a. The average ventilation was 16,000 cfm (205 cfm/brake horsepower)
b. Some of the sulfur dioxide is oxidized to sulfuric acid on the PVC filters used to collect these samples. Thus, the sulfate ion concentrations will be higher and the (ammonia/sulfate ion) ratios lower than those in the mine air.

$$NH_3 + H_2SO_4 \longrightarrow NH_4^+ HSO_4^- \quad [3]$$

This means that approximately a quarter of the hydrogen ions (acid hydrogens) in the sulfuric acid are consumed when the sulfuric acid is converted into ammonium hydrogensulfate. This reduces the concentration of the H^+ ion (the acidity) by 25%; the total acidity does not disappear because the HSO_4^- ion dissociates into H^+ and $SO_4^{=}$ ions in solution. As a result, one would find lower concentrations of sulfuric acid (a higher pH) and more sulfate ion on any respirable dust samples collected in the presence of ammonia.

Obviously, one cannot determine the amount of sulfuric acid in the air in an underground mine unless one does an analysis to determine the amount of ammonia on the filter and corrects for the loss of hydrogen ion through reaction with ammonia. This is accomplished in the following manner. If the aqueous extract from the silver membrane filter is acidic, ie., the pH is less than 7.00, we assume that all of the ammonia has reacted with the sulfuric acid in the mine air and formed ammonium hydrogensulfate and /or ammonium sulfate. The amount of sulfuric acid that the ammonia would have converted into the salts is then added to the amount of acid indicated by the pH analysis. This gives the total amount of sulfuric acid that is in the mine air. Dividing the amount of sulfuric acid by the amount of sulfate ion found in the sulfate ion analysis of the silver membrane filter, gives the percent of the sulfate ion formed by the catalytic purifier that exists as sulfuric acid in the mine air. Finally, the amount of sulfur dioxide in the mine air can be determined if a "Maskery Badge" (9) is placed behind the silver membrane filter in the sampling train. Measuring the sulfate ion trapped on the "Maskery Badge" (9) gives the amount of sulfur dioxide in the mine air and allows us to determine the fate of the fuel sulfur in the mine environment.

The presence of ammonia in the mine air raises interesting questions from an industrial health point of view. One of the concerns arising from the use of catalytic purifiers on diesels is that the catalysts produce sulfuric acid mists which could cause lung damage if the sulfuric acid reached the lung and was deposited on the lung tissue. The presence of ammonia in the mine environment would reduce the concern about the sulfuric acid because it can remove the acid from the mine air. An important question that has to be answered however, is when does the ammonia react with the sulfuric acid? If this reaction occurs very rapidly after the sulfuric acid is released from the diesel, then the amount of sulfuric acid and thus the

risk is reduced significantly. If the reaction occurs after the acid and the ammonia are drawn into the lungs of a miner, the damage caused by the sulfuric acid might occur before the acid reacted with the ammonia. Some data pertaining to this question was obtained in a study by Wilson and co-workers (10). These workers found that the ammonia generated in automobile exhaust was not completely neutralized (had not reacted completely with) the sulfuric acid released by the catalytic purifiers on cars by the time the exhaust gases were sampled 20 meters downwind from a roadway with a fairly high traffic density. Thus, the reaction between ammonia and sulfuric acid does not occur quickly in the open air. These results may not be relevant to the mine however, because the dilution of the exhaust gases would be much greater in the open air and the chance that an ammonia molecule would encounter a sulfuric acid molecule and react, would be low. It is more likely that the ammonia would be neutralized by the sulfuric acid in the mine because the two gases would be more concentrated in the enclosed environment of an underground mine and because the reaction between ammonia and sulfuric acid would occur instantaneously when the two molecules came together. Although this question cannot be answered at this time, it seems likely that the sulfuric acid in the mine air would be at least partially neutralized before it is inhaled. Although the answer is far from definite, the presence of ammonia in the mine environment would appear to reduce any concern arising from the presence of the sulfuric acid that is generated by the catalytic purifiers used in dieselized underground mines.

Finally, it is worth noting that the highest concentration of ammonia (ammonium ion) that was encountered during our study was only 0.46 mg/m^3. This concentration is far below the TLV concentration of 18 mg/m^3 for ammonia and even if all of the ammonia or ammonium ion had been in the form of ammonia, there would be no reason for concern. This is particularly true because our experience indicates that one cannot always detect ammonia in a muck pile. This obviously means that one need not have any concern because of the presence of ammonia in the air around a muck pile in the mine.

SULFURIC ACID CONCENTRATIONS IN THE MINE ENVIRONMENT

Once the filters to be used in collecting the respirable dust samples for the sulfuric acid and RCD analyses had been selected and the analytical procedures mastered, samples were collected under various conditions in several different mines to provide an overview of the sulfate ion (sulfuric acid) concentrations in the air in dieselized underground mines. In addition, samples were collected downstream from diesels burning different types of fuels and using various exhaust treatment devices. These studies demonstrate how these factors affect the concentration of sulfuric acid in the air downstream from diesels working in underground mines. The main objective of this investigation was to determine whether the diesel-generated sulfuric acid concentrations were high enough to cause health problems in miners working around and downstream from diesels in underground mines.

The Sulfate Ion Concentration in Dieselized Underground Mines

A large number of respirable dust and some total dust samples have been collected under various conditions in several different mines so that we could determine both the range and the average concentrations of sulfate ion (sulfuric acid) in dieselized underground mines. The data in Table 3 gives all of the sulfate ion concentrations found in seventeen different environments in four different underground nickel mines. Table 3 also presents the average sulfate ion concentration found in each mining environment and gives the sulfate ion concentration one would find if the ventilation had only been at the legal limit of 100 cfm/brake horsepower at each of the sampling sites.

The TLV value for sulfuric acid, the substance of concern in the mining environment, is 1.0 mg/m^3. Table 3 shows that the sulfate ion concentrations vary from a low of zero (in five samples) to a high of 3.40 mg/m^3 with only ten of the 75 samples (13%) having sulfate ion concentrations of greater than 1.0 mg/m^3. The average sulfate ion concentration in all 75 samples is only 0.49 ± 0.67 mg/m^3. Even if the ventilation in the mines had only been at the legal limit of 100 cfm/brake horsepower, the average sulfate ion concentration would only be 0.75 mg/m^3 and only 17 out of 75 samples would have a sulfate ion concentration in excess of the TLV value. Thus, the average concentration of sulfuric acid would not be at the TLV level even if all of the sulfate ion were present as sulfuric acid and the ventilation were at the legal limit. Because only a small portion of the sulfate ion appears to be present as sulfuric acid (*vide infra*) it would appear that there is no need to be concerned about diesel

Table 3 Sulfate ion concentrations in dieselized underground nickel mines where Deutz diesels were used.

Function Sampled Location	Exhaust Treatment Device	Ventilation cfm/brake horsepower	Sulfate ion concentration in mg/m^3	Average Sulfate ion Conc mg/m^3	Average Sulfate ion Concentration in mg/m^3 at a ventilation of 100 cfm/brake horsepower
Mucking, Hauling Stope A	PTX Catalyst	169	0.39, 0.36, 0.28	0.34	0.58
LHD cycle[a] Stope B	PTX Catalyst	205	1.70, 1.12, 2.31, 3.40, 1.60, 1.23, 1.51	1.84	3.77
LHD cycle Stope C	PTX Catalyst	256	0.30, 0.19, 0.48, 0.13, 0.19, 0.28, 0.43, 0.18, 0.20, 0.39, 0.43, 0.27, 0.54	0.31	0.80
LHD cycle Stope D	PTX Catalyst	256	0.04, 0.13, 0.27, 0.32, 0.18[b], 0.08[b], 0.26[b]	0.18[b]	0.47[b]
LHD cycle Drift A	PTX Catalyst	156	0.56, 0.36, 0.00	0.31	0.48
LHD cycle Drift B	PTX Catalyst	207	0.00, 0.00	0.00	0.00
Hauling, Dumping Drift C	PTX Catalyst	148	0.48[b], 0.37, 0.34, 0.26[b], 0.48, 0.89[b], 0.96[b]	0.54[b]	0.80[b]

Table 3 cont'd Sulfate ion concentrations in dieselized underground nickel mines where Deutz diesels were used.

Function Sampled Location	Exhaust Treatment Device	Ventilation cfm/brake horsepower	Sulfate ion concentration in mg/m^3	Average Sulfate ion Conc mg/m^3	Average Sulfate ion Concentration in mg/m^3 at a ventilation of 100 cfm/brake horsepower
LHD cycle Stope B	PTX Catalyst and a USBM Filter	205	3.12, 1.23, 2.18	218	4.47
LHD cycle Stope E	Johnson-Mathey Catalyst	110	0.23, 0.26, 0.53, 0.47, 0.13, 0.42, 0.13, 0.21	0.30	0.32
LHD cycle Stope E	Johnson-Mathey Catalyst plus a Fume Diluter	110	0.27, 0.30, 0.16	0.28	0.31
Mucking, Hauling Stope F	Corning Diesel Exhaust Filter	169	0.23, 0.04, 0.06	0.11	0.19
LHD cycle Stope E	Fume Diluter	110	0.17, 0.15, 0.12	0.15	0.16
LHD cycle Stope E	None	110	0.24, 0.00, 0.29, 0.16, 0.29, 0.03	0.17	0.19

Table 3 cont'd Sulfate ion concentrations in dieselized underground nickel mines where Deutz diesels were used.

Function Sampled Location	Exhaust Treatment Device	Ventilation cfm/brake horsepower	Sulfate ion concentration in mg/m^3	Average Sulfate ion Conc mg/m^3	Average Sulfate ion Concentration in mg/m^3 at a ventilation of 100 cfm/brake horsepower
Mucking, Hauling Stope F	none	169	0.16, 0.00	0.08	0.14
LHD cycle, Fuel A Drift D	none	156	0.10, 0.00	0.05	0.08
LHD cycle, Fuel B Drift D	none	156	0.31, 0.03	0.17	0.27
LHD cycle, Fuel C Drift D	none	156	0.28	0.28	0.44

a. LHD cycle means that the sample was collected downstream from the area where the diesel was mucking, hauling and dumping the ore in the stope.

b. Collected on PVC or Whatman GF/A filters. The sulfate ion concentrations may be too high.

generated sulfuric acid mists in dieselized underground nickel mines.

The Effect of Increasing the Sulfur Content of the Fuel

A few respirable dust samples that were collected on Whatman GF/A filters when three different fuels: a low sulfur, low aromatic Jet-A1 fuel, a regular No. 1 diesel fuel and a high sulfur, high aromatic 1990-type fuel, were burned in the diesel, were analyzed for sulfate ion. Although we were not able to collect enough samples to obtain definitive results, the sulfate ion concentrations in Table 4 suggest that more sulfate ion is found in the mine air when the sulfur content of the fuel is higher, ie., whilst the lowest average sulfate ion concentration was found when the regular No. 1 diesel fuel was used, the highest concentration of sulfate ion was found when the high sulfur 1990-type fuel was burned in the diesel. It is very tempting to assume that the very high (0.31 mg/m^3) concentration of sulfate ion found when the low sulfur Jet-A1 fuel was used, is in error and that the real sulfate ion concentration is close to the 0.03 mg/m^3 found in the other sample. Unfortunately, no error could be found in either of these analyses so this unexpectedly high sulfate ion concentration has been included in the table. Even with this value included however, the sulfate ion concentration was highest in the mine air when the fuel with the highest sulfur content is burned in the diesel. In spite of the results, it seems likely that the sulfur content of the fuel does influence the sulfate ion concentration in the mine air. Although the SO_2 analyses were not done because we were not aware of the "Maskery Badge" technique for measuring the SO_2 concentration in the mine air when these samples were collected, we would expect that the sulfur dioxide concentrations would also be much higher when a high sulfur fuel is burned in the diesels working in underground mines.

The Effect of Catalytic Purifiers, Filters and Fume Diluters

One aspect of this investigation was to learn how the sulfuric acid, the sulfate ion and the sulfur dioxide concentrations are affected by the different exhaust treatment devices that can be added to the exhaust train of the diesels used in underground mines. In this study, two different catalytic purifiers, a PTX and a new Johnson-Mathey catalyst, a Corning Diesel Exhaust filter and a fume diluter were tested. Each test involved comparing the sulfuric acid, the sulfate ion and the sulfur dioxide levels observed downstream from a diesel operating with and without a particular exhaust treatment device.

Table 4 The effect of the sulfur content of the fuel on the sulfate ion concentrations in the mine air.

Type of Fuel	Sulfur Content wgt. percent	Sulfate ion concentration* in mg/m^3	Average sulfate* ion concentration mg/m^3
Jet-A1 Fuel	0.007%	0.31 0.03	0.17
Regular #1 Diesel Fuel	0.085%	0.10 0.00	0.05
High Sulfur 1990 Type Fuel	0.490%	0.28	0.28

* a 180 horsepower F8L-714 Deutz diesel was mucking, transporting and dumping ore in a drift with an average ventilation of 29,000 cfm (156 cfm/brake horsepower).

All of the samples in this portion of the study were collected by drawing a known (approximately 2 litres/min) volume of air through a sampling train consisting of a nylon cyclone, a 25 mm. silver membrane filter and a 37 mm. filter holder containing an SO_2 adsorbing Maskery Badge, for a known length of time. This combination of filters collected the respirable-sized diesel particulate (soot), any sulfuric acid or sulfate salt that was in the mine air or adsorbed on the respirable-sized particulate and any gaseous sulfur dioxide that was in the mine air. The nylon cyclone was chosen because it is the method that is usually used to collect the respirable dust particles in the local mines. The respirable-sized particulate was collected because our previous work had shown that all of the sulfate ion in the nickel mine samples was in the respirable fraction (7) and because this is the fraction of the particulate that is of especial interest from an industrial health point of view. The silver membrane filter collected the respirable-sized particulate and any sulfuric acid and/or sulfate salts that were in the mine air or adsorbed on the particulate. The silver membrane filters were chosen because they did not introduce any errors into the analyses (vide supra). The Maskery Badge adsorbed and converted all of the sulfur dioxide that passed through the silver membrane filter into sulfate ion (9).

All of the analyses were carried out on the filter extracts. Since no ammonia was detected in any of these samples, analyzing the aqueous extract from the silver membrane filter for acid (pH) and for sulfate ion gave the amount of sulfate ion and the amount of sulfuric acid in the mine air at the sampling site. Analyzing the aqueous extract from the Maskery Badge for sulfate ion gave the amount of sulfur dioxide in the mine air at the sampling site. The sum of the sulfate ion concentrations on the Maskery Badge and the silver membrane filter gives the total amount of fuel-generated sulfur compounds in the air at the sampling site. Finally, these values were used with the percent sulfur in the fuel and the percent CO_2 in the intake air and the air at the sampling site, to estimate the sulfur balance, ie., to determine the percentage of the sulfur compounds in the fuel that were detected at the sampling site. The results of the individual analyses from the tests done using a 145 horsepower A6L-714 Deutz diesel at Falconbridge Nickel Mine Limited's Strathcona Mine and using a 195 horsepower F8L-714 Deutz diesel at Inco Metals Limited's Little Stobie Mine are in Tables 5 and 6, respectively.The average results for each exhaust treatment device are presented in Tables 7 through 9.

The Effect of Adding a Fume Diluter:- The results in Table 7 show that adding a fume diluter to the exhaust system of an A6L-714 Deutz diesel does not increase the amount of sulfate

Table 5. The pH and the sulfate ion concentrations on the silver membrane and Maskery Badges collected in a stope on the 2250 foot level of a nickel mine where a single 145 horsepower, A6L-714 Deutz diesel was mucking ore.

Exhaust Treatment System	Sulfate ion* concentration on the silver membrane filter mg/m^3	Sulfate ion* concentration on the Maskery Badge (SO_2) mg/m^3	Total* sulfate ion concentration mg/m^3	pH	Moles $H^+ \times 10^{-8}$ found	Moles $H^+ x10^{-7}$ expected if all the sulfate ion on the silver membrane was sulfuric acid	percent of the sulfate ion present as sulfuric acid
No Catalyst	0.034	0.253	0.287	6.38	0.626	2.71	2.3
	0.243	0.146	0.389	4.69	30.6	10.4	29
	0.00	0.784	0.784	4.68	31.3	0.00	0.00
	0.292	0.167	0.459	5.46	5.20	7.29	7.1
	0.288	1.025	1.313	5.30	7.52	4.79	15.7
Fume Diluter	0.151	0.501	0.652	5.08	12.5	25.2	5.0
	0.115	0.450	0.565	5.22	9.03	30.8	2.9
Johnson-Mathey Catalyst	0.227	0.714	0.941	4.83	22.2	27.9	8.0
	0.257	0.008	0.265	5.21	9.26	44.4	2.1
	0.532	0.256	0.788	5.47	5.08	85.4	0.59
	0.470	0.00	0.470	5.27	8.06	67.7	1.2
	0.127	1.44	1.567	5.35	6.70	28.7	2.3
	0.419	0.333	0.752	5.43	5.58	60.8	0.92
	0.125	0.043	0.168	5.42	5.70	22.3	2.6
	0.206	0.019	0.225	5.46	5.20	27.5	1.9
Johnson-Mathey Catalyst plus a Fume Diluter	0.272	0.207	0.479	5.08	12.5	45.8	2.7
	0.296	0.021	0.317	5.09	12.2	49.8	2.4
	0.157	0.120	0.277	4.97	16.0	26.4	6.1

* Ventilation was approximately 16,000 cfm(110 cfm/brake horsepower).

Table 6. The pH and the sulfate ion concentrations on the silver membrane and Maskery Badges collected on the 1400 foot level of a nickel mine where a single 195 horsepower, F8L-714 Deutz diesel was mucking ore.

Exhaust Treatment System	Sulfate ion* concentration on the silver membrane filter mg/m^3	Sulfate ion* concentration on the Maskery Badges (SO_2) mg/m^3	Total* sulfate ion concentration mg/m^3	pH	Moles $H^+ \times 10^{-8}$ found	Moles $H^+ \times 10^{-7}$ expected if all the sulfate ion on the silver membrane were sulfuric acid	percent of the sulfate ion present as sulfuric acid
No catalyst	0.160	0.183	0.343	5.24	8.62	13.5	6.4
Corning filter	0.232	0.00	0.232	5.24	8.62	18.8	4.6
	0.042	no Maskery badge		5.46	5.20	2.50	21
	0.060	no Maskery badge		5.29	7.72	3.75	20
PTX	0.391	0.331	0.722	5.23	8.84	25.8	3.4
Catalytic	0.359	0.00	0.359	5.16	10.4	11.4	9.1
Purifier	0.283	0.00	0.283	5.16	10.4	13.5	7.7

* Ventilation was approximately ± 33,000 cfm (169 cfm/brake horsepower).

Table 7. The effect of adding a fume diluter to the exhaust train of an A6L-714 Deutz diesel.*

Exhaust treatment system	Average sulfate ion on the silver membrane (mg/m^3)	Average SO_2 expressed as (mg/m^3 of sulfate ion on the Maskery Badge)	Average total sulfate ion (mg/m^3)	Percent $\left(\frac{\text{Sulfate ion}}{\text{Total sulfate ion}}\right)$	H^+ Moles $\times 10^{-7}$ expected if all the sulfate ion on the silver membrane were sulfuric acid	H^+ Moles $\times 10^{-8}$ found on the silver membrane	Percent sulfate ion present as sulfuric acid	Percent fuel sulfur compounds found as sulfuric acid at the sampling site
No catalyst	0.171±0.14	0.475±0.40	0.646±0.42	26.4	5.04±4.0	15.0±15	13.5±11.7 (6.4)**	2.8
Fume diluter	0.133±0.02	0.476±0.04	0.608±0.06	21.9	28.0±4	10.8±2.4	3.95±1.5	0.86
Johnson-Mathey Catalyst	0.295±0.16	0.352±0.50 (0.196)**	0.647±0.47 (0.49)**	45.6 (60)**	45.6±23	8.47±5.7	2.45±2.3	1.1
Johnson-Mathey Catalyst plus Fume Diluter	0.242±0.07	0.116±0.09	0.358±0.11	67.6	40.7±12	13.6±2.1	3.73±2.1	2.5

* The averages in this table were calculated from the data in Table 5.

** The value after excluding the samples with extremely small amounts of Sulfate ion in Table 5. We believe that this value is more accurate than the number above the bracket.

ion in the exhaust. This effect is observed whether the fume diluter is added to the bare engine (see rows 1 and 2) or whether the fume diluter is added to the engine fitted with the Johnson-Mathey catalyst (see rows 3 and 4). In fact, the amount of sulfate ion decreases by approximately 20% when the fume diluter is added to the exhaust system in both cases. Presumably, this occurs because the fume diluter pulls in extra mine air to dilute the exhaust. This would lower the concentration of the sulfate ion in the exhaust and therefore in the mine air at the sampling site. The failure to observe an increase in the amount of sulfate ion when the fume diluter was added to the exhaust system is not surprising because the fume diluter simply adds mine air (dilutes) the exhaust and would not be expected to oxidize any of the sulfur dioxide to sulfur trioxide (sulfate ion and/or sulfuric acid).

Although the percentage of the (sulfate ion/Total sulfate ion) is unchanged when the fume diluter is added to the bare engine as one would expect, it appears that the same trend is not observed when the fume diluter is added to the engine fitted with the Johnson-Mathey catalyst. We believe that the results are comparable however. An examination of the results in Table 5 shows that the high sulfate ion concentration on the Maskery Badges is due to one very high result (1.44mg/m^3). If this value is discarded, the average sulfate ion concentration on the Maskery Badges is only 0.196 mg/m^3, ie., is almost identical to that observed when the diesel has both the fume diluter and the Johnson-Mathey catalyst in the exhaust train. Since discarding the very high result is reasonable on a statistical basis, we have concluded that the numbers in the brackets in row 3 of Table 7 are the numbers that should be used in this comparison. This means that adding the fume diluter does not alter the sulfate ion-sulfur dioxide mixture in the exhaust significantly. The much higher percent (sulfate ion/ Total sulfate ion) found when the catalyst is on the diesel, ie., 64% when the catalyst is present and only 24% when the no catalyst is used, is observed because the catalyst converts more of the sulfur dioxide into sulfate ion.

The results in column 8 of Table 7 also appear to contradict one another. Adding the fume diluter seems to reduce the percentage of (sulfuric acid/sulfate ion) markedly in one experiment but has little or no affect on the percentage of sulfuric acid in the exhaust in the second case. We believe the different responses arise because there is an error in the sulfate ion analyses of the silver membrane filters. In the samples where no catalyst was used, the sulfate concentrations were below the calibration range of the assay and we do not believe that the amounts of sulfate ions found in these analyses are accurate. Since a small error in the sulfate ion concentration can cause a large error in the percent (sulfuric acid/

sulfate ion), the (sulfuric acid /sulfate ion) percentages based on these values should not be used to assess the effect of adding a fume diluter to a Deutz diesel. If these values are replaced by an average no catalyst value, ie., the 6.4% value in the brackets in column 8, adding the fume diluter does not seem to have a significant effect on the amount of sulfuric acid in the exhaust, ie., the percent (sulfuric acid/sulfate ion) decreases by 60% when the fume diluter is used in the first experiment and increases by approximately 50% in the second experiment.Thus, when the questionable percentages are not used in calculating the effect of the fume diluter, the average effect of adding the fume diluter is to all intents and purposes, zero. Although more samples would have to be collected to prove this point, we do not believe that adding the fume diluter affects the percentage of sulfate ion that exists as sulfuric acid significantly.

Finally, this conclusion is supported by the observation that the fume diluter does not affect the percentage of the sulfur compounds in the fuel that exist as sulfuric acid at the sampling site, column 9. In fact, the average percent of fuel-generated sulfur compounds that exist as sulfuric acid at the sampling site with and without the fume diluter, ie., 2% $\pm$ 0.9% and 1.7% $\pm$ 0.8%, respectively, are identical within the limits of the analysis. This expected result confirms the conclusion that adding a fume diluter does not affect the percent of (sulfuric acid/sulfate ion) in the exhaust. If the fume diluter does not alter the amount of sulfate ion or the percentage of sulfuric acid in the exhaust, it cannot affect the percentage of fuel-generated sulfur compounds that exist as sulfuric acid at the sampling site.

The Effect of Adding a Catalytic Purifier:- An examination of the results in Table 8 shows that adding a platinum-based (oxidizing type) catalytic purifier to the exhaust system of a Deutz diesel increases the amount of sulfate ion in the exhaust significantly. In fact, the amount of sulfate ion increased by an average of 73% when the Johnson-Mathey catalyst was added to the bare engine of a 145 horsepower A6L-714 Deutz diesel. Similar results were observed when a Johnson-Mathey catalyst was added to the A6L-714 Deutz diesel fitted with a fume diluter, ie., the sulfate ion was on average, 82% higher when the catalytic purifier was used. When a PTX catalytic purifier was added to the exhaust system of the 195 horsepower F8L-714 Deutz diesel, the sulfate ion increased by an average of 115%. In fact, the amount of sulfate ion captured on the silver membrane filter almost doubles, ie., it increases by an average of 90% $\pm$ 22%, when a Johnson-Mathey or a PTX catalyst is installed on a Deutz diesel. The effect of the catalyst is even more apparent if one compares the (sulfate ion/Total sulfate ion) ratios for the engines operating with and without an oxidizing type of catalyst, column

Table 8. The effect of adding a catalytic purifier to the exhaust system of Deutz diesels.*

Exhaust treatment system	Average sulfate ion on the silver membrane (mg/m^3)	Average SO_2 expressed as mg/m^3 of sulfate ion on the Maskery Badge	Average total sulfate ion (mg/m^3)	Percent $\frac{(\text{Sulfate ion})}{(\text{Total (Sulfate ion)})}$	H^+ Moles $\times 10^{-7}$ expected if all the sulfate ion on the silver membrane were sulfuric acid	H^+ Moles $\times 10^{-8}$ found on the silver membrane	Percent sulfate ion present as sulfuric acid	Percent fuel sulfur compounds found as sulfuric acid at the sampling site
A stope on the 2250 foot level of a nickel mine where a single 145HP A6L-714 Deutz diesel was mucking ore:								
No Catalyst	0.171±0.14	0.475±0.40	0.646±0.42	26.4	5.04±4.0	15.0±15	13.5±12 (6.4)**	2.8
Johnson-Mathey Catalyst	0.295±0.16	0.352±0.50 (0.196)**	0.647±0.47 (0.49)**	45.6 (60)**	45.6±23	8.47±5.7	2.45±2.3	1.1
Fume Diluter - No Catalyst	0.133±0.02	0.476±0.04	0.608±0.06	21.9	28.0±4.0	10.8±2.4	3.95±1.5	0.86
Fume Diluter plus Johnson-Mathey Catalyst	0.242±0.07	0.116±0.09	0.358±0.11	67.6	40.7±12	13.6±2.1	3.73±2.1	2.5
A stope on the 1400 foot level of a nickel mine where a single 195HP F8L-714 Deutz diesel was mucking ore:								
No Catalyst	0.160	0.183	0.343	46.6	13.5	8.62	6.4	3.0
PTX Catalyst	0.344±0.06	0.110±0.19	0.455±0.24	75.6	16.9±7.8	9.88±0.90	6.73±3.0	5.1

* The averages in this table were calculated from the data in Tables 5 and 6.

** The value after excluding the samples with extremely small amounts of sulfate ion in Tables 5 and 6. We believe that this value is more accurate than the number above the bracket.

5, Table 8. The percentage of (sulfate ion/Total sulfate ion) in the exhaust jumps from an average of approximately 24% with no catalyst to approximately 64% when a Johnson-Mathey catalyst is used on the diesel. A similar increase from 47% to 76% is observed when a PTX catalyst is added to the exhaust system. These results clearly demonstrate that the catalyst does oxidize (convert) a significant portion of the sulfur dioxide in the exhaust into sulfate ion (sulfuric acid).

The increased amounts of sulfate ion found when the catalysts are used are not unexpected.In fact, several other groups have reported that the platinum-based (oxidizing) type of catalyst increases the amount of sulfate ion in the exhaust. For example, Sharp (1) found that the sulfate ion in the raw exhaust increased by nine times, ie., from 6.7 mg/m^3 when no catalyst was used to 62 mg/m^3 when a PTX catalyst was added to the exhaust train of a 3304 PC-T Caterpillar diesel and Lawson et. al. (2) reported that the sulfate ion emissions increased by 50% when a platinum-based PTX catalyst was added to a Deutz diesel. The increases of 73%, 82% and 115% (an average of 90%) found in the mine seems reasonable because the results are close to those found in laboratory studies for a Deutz diesel and because they are bracketed by the published data (1,2).

The most interesting observation however, is that the percent of sulfate ion present as sulfuric acid and the percentage of fuel sulfur compounds that exist as sulfuric acid are not increased by adding a catalytic purifier to the exhaust train of the diesel. In fact, if the more correct value of 6.4% is used for the bare A6L-714 Deutz diesel (vide supra), the percentage of (sulfuric acid/sulfate ion) decreases slightly in one case and does not change in the second case when the Johnson-Mathey catalyst is used on the A6L-714 Deutz diesel and is unchanged when the PTX catalyst is added to the exhaust of the F8L-714 Deutz diesel. Thus the average (sulfuric acid/sulfate ion) percentages for the bare engine and the catalyst are identical within the experimental error of the method, ie., the average is 5.6% $\pm$ 1.4% without a catalyst and 4.3% $\pm$ 2.2% when the diesel has a catalyst in the exhaust system. Thus, adding a catalyst does not seem to affect the percentage (sulfuric acid/sulfate ion) in the exhaust significantly. The same effect is observed when one examines the percentage of sulfur compounds in the fuel that exist as sulfuric acid at the sampling site. The average percent sulfuric acid is 2.2% $\pm$ 1.2% when no catalyst is used and is 2.9% $\pm$ 2.0% when a catalyst is in the exhaust system of the diesel. Again, the results are identical within experimental error and one is again forced to conclude that the catalyst does not affect the percentage of sulfuric acid in the mine air. Thus, the results in the last two columns of Table 8 are

in agreement. It should be noted however, that the absolute amount of sulfuric acid would still be higher in the mine air when a catalyst is used because a catalyst almost doubles the amount of sulfate ion and therefore sulfuric acid, in the exhaust.

The Effect of Adding a Corning Diesel Exhaust Filter:- Table 9 shows that the amount of sulfate ion does not increase when a Corning Diesel Exhaust filter is added to the exhaust system of the 195 horsepower F8L-714 Deutz diesel. In fact, the sulfate ion seems to be approximately 30% lower when the Corning filter is used. However, only a single sample was analyzed for the bare engine and we cannot be certain that adding the Corning filter decreases the amount of sulfate ion in the exhaust. In any case, the Corning filter does not seem to increase the amount of sulfate ion in the exhaust. This result was anticipated because the Corning filter does not contain any platinum and is not an oxidizing type of filter.

The Total sulfate ion and the percent (sulfate ion/Total sulfate ion) were not calculated for the Corning filter because the sulfur dioxide concentrations were believed to be in error, ie., no sulfate ion was found on the Maskery Badges suggesting that there was no sulfur dioxide in the mine air. However, the fuel used during the Corning filter tests had a higher sulfur content than the fuels used in any other test and we concluded that the sulfate ion analysis of the Maskery Badges was in error. As a result, we did not carry out any calculations using these values.

The surprising result was that the percent sulfate ion that was present as sulfuric acid was 2.4 times higher when the Corning filter was installed on the diesel. However, two of the samples that were used to calculate the average precent (sulfuric acid/sulfate ion) for the Corning filter were collected for a very short time and had very small amounts of sulfate ion. In fact, the sulfate ion concentrations on these two silver membrane filters were below the concentrations that could be measured accurately. If the percent (sulfuric acid/sulfate ion) for these samples are not used, the percent (sulfuric acid/sulfate ion) is only 4.6% or is within 30% of the value found when no filter was used. This leads one to conclude that the Corning filter probably does not affect the percent of (sulfuric acid/sulfate ion) in the exhaust significantly. In fact, we would expect the percentage of sulfuric acid from the bare engine and the Corning filter to be identical because the Corning filter does not oxidize sulfur dioxide to sulfur trioxide (sulfuric acid). Unfortunately, only two samples were used in arriving at this conclusion and more data would have to be collected before we could be certain that the Corning filter does not affect the percentage of sulfuric acid in the exhaust significantly.

Table 9. The effect of adding a Corning Diesel exhaust filter to the exhaust system of an F8L-714 Deutz diesel.*

Exhaust treatment system	Average sulfate ion on the silver membrane (mg/m^3)	Average SO_2 expressed as mg/m^3 of sulfate ion on the Maskery Badge	Average total sulfate ion (mg/m^3)	Percent $\left(\frac{\text{Sulfate ion}}{\text{Total (Sulfate ion)}}\right)$	H^+ Moles $\times 10^{-7}$ expected if all the sulfate ion on the silver membrane were sulfuric acid	H^+ Moles $\times 10^{-8}$ found on the silver membrane	Percent sulfate ion present as sulfuric acid	Percent fuel sulfur compounds found as sulfuric acid at the sampling site
No Catalyst	0.160	0.183	0.343	46.6	13.5	8.62	6.4	3.0
Corning Filter	0.111±0.10	0	-	-	8.35±9.1	7.18±1.8	15.2±9 (4.6)**	-

* The averages in this table were calculated from the data in Table 6.

** The average value after excluding the samples with extremely small amounts of sulfate ion in Table 6. We believe this value is more accurate than the number above the bracket.

Conclusions:-Only the oxidizing or platinum-based catalysts cause a significant increase in the amount of sulfate ion in the exhaust. Although the exhaust from a diesel fitted with a Corning filter or a fume diluter appears to have slightly less sulfate ion, it appears that the fume diluter and the Corning Diesel Exhaust filter do not alter the sulfate ion or the sulfuric acid concentration in the exhaust significantly.

One surprising result was that only a small amount of sulfuric acid was detected downstream from a diesel, even when the diesel had an oxidizing type of catalyst in the exhaust train. In fact, the percentage of the sulfate ion that is present as sulfuric acid (using only the correct values in column 8 of Tables 5 and 6) only ranges from 9.1% to 0.6% with an average value of only 3.8% $\pm$ 2.6%. This result was surprising because other workers have stated that adding a catalytic purifier to the exhaust system increases the amount of sulfuric acid in the exhaust markedly. It is worth noting however, that most of these workers have analyzed for sulfate ion and have not demonstrated that the sulfate ion is present as sulfuric acid. We believe that the combination of the pH and sulfate ion analyses show that very little of the sulfate ion is actually present as sulfuric acid.

This conclusion is supported by the results that were obtained when the amount of sulfuric acid in the mine air at the sampling site was expressed as a percentage of the total sulfuric acid one would have expected if all of the sulfur-containing compounds in the fuel had been converted into sulfuric acid. The maximum amount of sulfuric acid that one would have expected at the sampling site was calculated from the sulfur content of the fuel and the percent CO_2 in the intake air and the air at the sampling site, Table 10. When this was done, the results (see Tables 7-9) showed that the same percentage of sulfur compounds in the fuel (sulfur dioxide) was converted into sulfuric acid when the diesel was operating with and without an oxidizing type of catalytic purifier, ie., the results suggest that only 1.8% $\pm$ 1.0% of the sulfur dioxide generated in the engine had been converted into sulfuric acid in the 145 horsepower A6L-714 Deutz diesel and that only 4.1% $\pm$ 1.0% of the sulfur dioxide had been converted into sulfuric acid by the 195 horsepower F8L-714 Deutz diesel. The average amount of sulfur compounds in the fuel that is converted into sulfuric acid by the two Deutz engines is 2.6 $\pm$ 1.5%. Again, the results show that the percentage of sulfur compounds in the fuel which are converted into sulfuric acid is within experimental error, the same whether or not the diesel has a catalytic purifier in the exhaust train.

Two other studies have determined the percent conversion of fuel sulfur into sulfuric acid. Wilson and co-workers (10) reported that 13 $\pm$ 3% of the fuel sulfur was converted into

Table 10. The maximum concentration of sulfate ion expected when Deutz diesels fitted with different exhaust treatment devices were mucking ore in a stope.

	% CO_2 at the Sampling Site	% CO_2 in the Intake Air	Net Percent CO_2	% Sulfur in Fuel	Mg. Sulfate Ion expected at the Sampling Site if all the Fuel Sulfur were converted into Sulfate Ion (mg/m^3)
In a stope on the 2250 foot level where a single 145 HP A6L-714 Deutz diesel was mucking ore:					
No Catalyst	0.095	0.035	0.060	0.08	0.91
	0.104	0.035	0.069	0.08	1.04
	0.105	0.035	0.070	0.08	1.06
Fume Diluter No Catalyst	0.107	0.035	0.072	0.09	1.23
	0.127	0.035	0.092	0.09	1.57
	0.112	0.035	0.077	0.09	1.31
	0.135	0.035	0.100	0.09	1.70
Johnson-Mathey Catalyst	0.120	0.035	0.085	0.08	1.29
	0.120	0.035	0.085	0.08	1.29
	0.103	0.035	0.068	0.09	1.56
	0.096	0.035	0.061	0.09	1.04
Johnson-Mathey Catalyst plus Fume Diluter	0.147	0.035	0.112	0.05	1.06
	0.153	0.035	0.118	0.05	1.12
	0.146	0.035	0.111	0.05	1.05
In a stope on the 1400 foot level where a single 195 HP F8L-714 Deutz diesel was mucking ore:					
No Catalyst	0.160	0.109(b)	0.054	0.20	2.04
	0.166	0.109(b)	0.057	0.20	2.16
	0.176	0.109(b)	0.067	0.20	2.53
PTX Catalyst	0.165	0.115	0.050	0.20	1.89
	0.185	0.115	0.070	0.20	2.65
	0.175	0.125	0.050	0.20	1.89
Corning Diesel Exhaust Filter	0.202	0.095(a)	0.107	0.22	4.45
	0.202	0.095(a)	0.107	0.22	4.45
	0.172	0.105(a)	0.067	0.24	3.04

a. Measured by M. Ghangal, CANMET, Belle's Corners, Ontario.
b. Average percent CO_2 found in the intake air of this mine. The actual values were not measured.
c. The fuel analyses were done in the CANMET Laboratories at Belle's Corners, Ontario.
d. The mg/m^3 sulfate ion at the sampling site was calculated using the formula:-

$$mg/m^3 \text{ sulfate ion at sampling site} = \frac{(\%S \text{ in fuel})(\text{Net } \% CO_2)\ (12 \times 96 \times 1000)}{32 \times 85 \times 100 \times 22.4}$$

sulfuric acid by the catalysts used in cars. This study is interesting because it is the only study where the sulfate ion analysis only detected sulfuric acid and not sulfate ion. In this study only the sulfuric acid released when the particulate filter was heated to 130°C, was analyzed. The volatile sulfate was undoubtedly sulfuric acid because inorganic sulfate salts would not volatalize at this temperature. In another study Pierson and co-workers (11) found that only 1.4 ± 1.1% of the sulfur dioxide formed from the sulfur compounds in the gasoline burned in cars and only 2.4 ± 0.3% of the sulfur dioxide formed from the sulfur compounds in the diesel fuel burned in trucks, was oxidized to sulfate ion (sulfuric acid) by the catalytic converters installed on these vehicles. This study was carried out in tunnels along the Pennsylvania Turnpike where the air flow (dilution of the exhaust gases) would be expected to be similar to those observed in a mining environment. In any case, the excellent agreement between the percent conversion of the sulfur in diesel fuel into sulfuric acid, found in the tunnel (2.4%) and in the mine (2.6%), is striking. The higher values found by Wilson et. al. in the highway study suggest that some of the sulfur dioxide is being oxidized to sulfuric acid in the air. In any case, all three studies force one to draw the same conclusion, ie., that only a very small percentage of the fuel sulfur is converted into sulfuric acid by the oxidizing catalysts used in both surface (10,11) and underground vehicles. In fact, it appears that only 2.6 ± 1.5 % of the sulfur dioxide formed from the sulfur compounds when the fuel is burned in a Deutz diesel, exists as sulfuric acid at the sampling site in nickel mines. It is worth noting that this conclusion was reached when no ammonia was detectable. Obviously, the amount of sulfuric acid would be even lower if ammonia were present in the mine environment.

Finally, sulfuric acid is undoubtedly produced in the catalytic purifier when the sulfur trioxide that is formed by the catalyst, reacts with the water in the hot exhaust gases. It is important therefore, to try to rationalize the low percentages of sulfuric acid in the mine air. One possibility is that the very hot and corrosive sulfuric acid might react with the metal support for the platinum catalyst to form a small particle of a metal sulfate and water. This small particle of sulfate salt would be on the surface of the catalyst where it would be exposed to a high velocity stream of exhaust gases. The exhaust gases would undoubtedly sweep the small particle of sulfate salt out of the catalyst into the mine air where it could be detected as sulfate ion but not as sulfuric acid. We had two silver membrane filters analyzed for aluminum, because the major component of the support phase of the catalyst was aluminum. Unfortunately, the aluminum levels in the filters that were analyzed were too low to detect. Since a calculation showed that the amount of aluminum would still have been below the detection limit even if all of the sulfate ion had been in the form of aluminum sulfate, the tests were

inconclusive. Obviously, larger samples would have to be collected to test this hypothesis correctly.

A second possibility is that the sulfuric acid reacts with the finely divided (respirable) particles of ore converting the metal sulfides in the ore into metal sulfates. If this occurred either in the mine air or on the filter during the time the sample was collected, the sulfuric acid would be in the form of a metal sulfate when it was analyzed. This last method of consuming the sulfuric acid, ie., of converting the sulfuric acid into sulfate salts, is certainly possible because 45% of the respirable dust (vide infra) collected in the local nickel mines is mine dust (ore). Unfortunately, we have not been able to determine the rate of reaction between sulfuric acid and finely divided particles of ore and are therefore, unable to suggest which if any, of these alternatives is correct. It would however, be interesting to determine the (sulfuric acid/sulfate ion) ratios at various distances from a stationary diesel in a drift so that we could learn whether the sulfuric acid reacts with the ore to form sulfate salts.

In fact,it is critical to determine when the sulfuric acid is neutralized in the mine environment.If the sulfuric acid is neutralized in the catalyst, ie., the (sulfate ion/sulfuric acid) ratio in the exhaust is that found in the pH and sulfate ion analyses, miners working around or downstream from the diesel would never be exposed to significant concentrations of sulfuric acid. If the sulfuric acid is neutralized in the mine air by reaction with the respirable-sized particles of ore, the miner might be exposed to concentrations of sulfuric acid which could occasionally reach the TLV value. Finally, if the reaction between the sulfuric acid and the ore were slow and occurred on the silver membrane filter, the miners working downstream from the diesel would be exposed to the sulfuric acid released by the diesel. Although we have not been able to do any experiments to determine where the sulfuric acid is converted into sulfate ion, the similar (sulfuric acid/sulfate ion) ratios found in the mine air and downstream from surface vehicles in tunnels and highways (10,11), make it almost certain that a significant amount of the sulfuric acid must exist as sulfate ion in the mine air. If this is the case, it is highly unlikely that the concentrations of sulfuric acid in the mine air would ever reach the TLV concentration for sulfuric acid.

A Material Balance for the Sulfur Compounds in Diesel Fuel

The results from the sulfur analyses of the fuels used during these tests and the CO_2 concentrations in the intake air and at the sampling site were used to estimate the amount of sulfate ion that should have been detected at the sampling site if all of the fuel sulfur

had been converted into sulfate ion, Table 10. Then, these quantities were used to estimate the material balance for the sulfur compounds in the fuel. Since all of the sulfur compounds in the fuel must show up as either sulfuric acid, sulfate ion or sulfur dioxide, the total sulfate ion found on the silver membrane filter and the Maskery Badge accounts for all of the fuel-related sulfur compounds that were collected at the sampling site. Dividing the total sulfate ion found on the silver membrane filters by the sulfate ion concentrations predicted in Table 10 gives the percentage recovery of the sulfur compounds in the fuel at the sampling site, Table 11. The results show that the material balance (the percentage of the sulfur compounds in the fuel that were detected at the sampling site) is not good. In fact, the average percent recovery is only 47 $\pm$ 13% in the nickel mine where the low sulfur fuel was used and is only 13 $\pm$ 9% in the nickel mine where a higher sulfur fuel was burned. In spite of the low percent recovery of the fuel-generated sulfur compounds, the general agreement between the results of this and other studies (10,11, vide supra) suggests that the results of this study are representative of the sulfur distribution in the mine air.

It is interesting to speculate on the reason for the very different recoveries of the fuel-generated sulfur compounds in the two mines. In the first mine, the samples were collected in a stope that was set aside for our studies. In this case, the stope was fairly dry even though the muck pile was wet down from time to time in an effort to reduce the dust. In the mine where the average recovery was only 13% the stope was wet and the humidity near 100%. Thus, it appears that the humidity in the mine might play an important role in determining the fate of any sulfuric acid that is released in the diesel exhaust. The much lower recovery of the fuel-generated sulfur compounds in the humid mine environment begs the question as to where the sulfuric acid, the sulfur dioxide and/or the sulfate ion goes in the humid mine. One possibility is that the sulfuric acid reacts with the high concentration of water in the mine air to form a droplet of a dilute sulfuric acid solution. This droplet would be heavier than air and would settle out of the mine air very quickly. Sulfur dioxide is also extremely soluble in water and could suffer the same fate. If this occurred, the sulfur compounds produced from the sulfur compounds in the fuel would not be found by our sampling technique. If this is the reason that sulfuric acid is not found in the mine air, then the concern for occupational exposure to sulfuric acid is further reduced in humid mines, ie., most of the sulfuric acid would not be in the air where it could be drawn into a miner's lung in a humid mine. It is important to note in considering this argument, that the samples in this study were collected while the diesel was operating between 10 and 200 feet from the sampling station. Thus, if this settling phenonmenon is responsible for the low recovery of the fuel sulfur comounds, the sulfur

Table 11. The sulfur balance in the nickel mines.

Exhaust treatment system	Average sulfate ion on the silver membrane (mg/m^3)	Average total* sulfate ion expected (mg/m^3)	Percent Recovery $\left[\frac{\text{Sulfate ion}}{\text{Total sulfate ion expected}}\right]$
A stope on the 2250 foot level of a nickel mine where a single 145 HP A6L-714 Deutz diesel was mucking ore.			
No catalyst	0.646±0.42	1.003±0.08	64
Fume diluter	0.608±0.06	1.452±0.22	42
Johnson-Mathey catalyst	0.647±0.47	1.295±0.21	50
Johnson-Mathey catalyst plus fume diluter	0.358±0.11	1.077±0.04	33
			Average 47±13
A stope on the 1400 foot level of a nickel mine where a single 195 HP F8L-714 Deutz diesel was mucking ore.			
No catalyst	0.343	2.243±0.26	15
PTX catalytic purifier	0.111	2.143±0.44	3
Corning filter	0.455±0.24	3.980±0.81	21
			Average 13±9

* These values were calculated in Table 10.

compounds must drop out of the mine air extremely rapidly and it would be almost impossible for a miner to be exposed to (breathe) significant quantities of a sulfuric acid mist. Furthermore, any acid that the miner did breathe in a humid mine would almost certainly be in the form of a dilute aqueous solution that is much less dangerous than a pure sulfuric acid mist. This would reduce the concern for the miner even more.

Sulfuric Acid Aerosols and Industrial Health

The work in this section of the report shows that the sulfate ion concentrations are reasonably low in the air of dieselized underground mines. In fact, even if all of the sulfate ion in the mine air were present as sulfuric acid, the TLV of sulfuric acid would only be reached in a very few instances. This does not mean that there is a health problem however, because only a very small percentage of the sulfate ion on the silver membrane filters is present as sulfuric acid and because it seems likely that a significant percentage of the sulfuric acid is present as sulfate ion in the mine air. The exposure to sulfuric acid is of even less concern when ammonia is present in the mine air as this would further reduce the the concentration of sulfuric acid in the mine air. This, coupled with the rapid settling out of the fuel-generated sulfur compounds in the humid mine air, should make it virtually impossible to find levels of sulfuric acid which are anywhere near the TLV value in the local nickel mines. In conclusion, we do not believe that diesel generated sulfuric acid mists presents any health problems for nickel miners working near Deutz diesels regardless of the type of catalytic purifier or filter that is used in the exhaust train of the diesel. Although this statement cannot be extended directly to all mines, the very small percentage of fuel-generated sulfur compounds that exist as sulfuric acid in the nickel mines suggest that sulfuric acid mists would not cause a problem in any mining environment.

RESPIRABLE COMBUSTIBLE DUST (RCD) SAMPLES IN DIESELIZED MINES

The Composition of the RCD

Several respirable dust samples were collected along side the sulfate ion samples in underground mines so that we could gain some insight into the amounts of respirable dust and respirable combustible dust (an RCD) in dieselized underground mines. The respirable dust (RCD) samples were collected by drawing a known volume of air (usually 2 litres/min.) through a 25 mm. silver membrane filter for a known length of time. The value of the RCD was the loss in weight that occurred when the 25 mm. silver membrane filter was heated in an oven for one hour at 400 ^{o}C (752 ^{o}F). This was the maximum temperature that could be used for measuring the RCD for these samples because the silver membrane filters lose weight (volatalize) when they are heated to more than 400^{o}C (12). The data in Tables 12-15 show the concentrations of some of the components of the respirable dust samples collected in several different dieselized underground mines.

The amount of PAHs found in seventy-one different mining environments in several different types of mines and under numerous different conditions are shown in Table 12. These results which express the PAHs as a percentage of the weight of the extract from Hi Vol filters collected in underground mines, have been included because the weight of the Hi Vol extracts and the respirable combustible dust should be similar, ie., the hydrocarbon material in the extract from a Hi Vol filter is adsorbed on the respirable-sized particulate (3) and is all combustible. This means that all of the extractable material (the soluble organic fraction or SOF) would be lost from a silver membrane filter when it was heated in the RCD experiment. If the soluble organic fraction (SOF) constitutes a significant fraction of the RCD as one would expect, the weight of the Hi Vol extract and the RCD should be similar and expressing the PAHs as a percentage of the extract weight from the Hi Vol filters should provide a fair to good estimate of the PAH contribution to the RCD weight. The results in Table 12 show that the PAHs only represent between 0.44% and 0.006% (an average of 0.069% $\pm$ 0.08%) of the Hi Vol extract weight. Thus, the PAHs can only account for approximately 0.07% of the RCD weight and do not constitute a significant portion of the respirable combustible dust (RCD).Unfortunately, the same cannot be said from a health point of view. The PAH fraction of the RCD contains most of the compounds that have made scientists worry about workers who breathe diesel exhaust (13,14). Finally, it is worth noting that the difficulty in analyzing

Table 12. An estimate of the percentage of PAHs in RCD samples.

Sample	Total PAHs ng/m^3	Wt of Extract mg	Volume m^3	%Wt of Total PAHs in extract
Uranium Mine	25.9	38.45	326.21	0.022
Detroit Diesel	32.4	66.21	490.89	0.024
PTX Catalyst	30.8	79.23	491.58	0.019
	85.4	134.39	550.95	0.035
	84.7	175.01	531.75	0.026
Nickel Mine	27.4	34.85	365.45	0.029
Deutz Diesel	26.3	19.83	421.21	0.056
PTX Catalyst	26.4	49.13	419.64	0.022
	60.0	13.53	254.57	0.113
	68.4	23.09	226.04	0.067
	30.7	26.22	216.00	0.025
Salt Mine	420 .	14.48	29.32	0.085
Caterpillar Diesel	60.9	41.06	286.31	0.042
PTX Catalyst	300	13.17	44.73	0.102
	96.4	49.19	222.40	0.043
	190	13.10	31.15	0.045
	3.95	27.15	2587.95	0.038
Nickel Mine	197	86.04	106.66	0.024
Deutz Diesel	101	83.13	132.33	0.016
PTX Catalyst				
Nickel Mine	209	73.27	140.34	0.040
Deutz Diesel	155	113.36	193.64	0.026
PTX Catalyst plus a U.S.B.M. filter				

Table 12. An estimate of the percentage of PAHs in RCD samples.
Cont'd

Sample	Total PAHs ng/m^3	Wt of Extract mg	Volume m^3	% Wt of Total PAHs in extract
Nickel Mine	106	37.59	103.30	0.029
Deutz Diesel	65.9	13.25	86.03	0.043
PTX Catalyst	111	29.25	146.11	0.055
	154	21.44	107.04	0.077
Uranium Mine	454	25.32	21.63	0.039
Detroit Diesel	173	3.80	21.63	0.098
No Catalyst	538	41.44	34.62	0.045
	212	64.88	52.67	0.017
Drill Oil	175	14.62	272.78	0.326
	344	397.6	272.78	0.024
Blasting Fumes	921	21.52	31.77	0.136
	4299	147.63	82.15	0.239
	1651	209.04	62.44	0.049
Nickel Mine	26.7	51.33	492.86	0.026
Deutz Diesel	23.6	72.27	559.91	0.018
	58.3	88.57	444.79	0.029
	117	320.95	469.44	0.017

Table 12. An estimate of the percentage of PAHs in RCD samples.
Cont'd

Sample	Total PAHs ng/m^3	Wt of Extract mg	Volume m^3	% Wt of Total PAHs in extract
Nickel Mine Deutz Diesel	24.7	34.85	365.45	0.026
	27.8	13.60	551.59	0.113
	13.4	12.28	556.78	0.061
	54.0	16.50	361.89	0.118
	80.5	20.33	265.05	0.105
	40.5	7.83	303.84	0.157
	14.7	15.5	327.91	0.031
	20.4	32.7	345.68	0.021
	6.82	6.65	493.76	0.051
	9.69	5.26	406.18	0.075
Ambient Air Samples	4.04	3.35	704.58	0.085
	15.0	5.37	563.34	0.157
	4.7	12.09	2598.25	0.101
	13.1	20.01	2562.35	0.168
	29.9	20.73	561.95	0.081
	14.7	59.11	1571.73	0.039
	67.2	18.41	746.9	0.273
	10.2	4.11	475.72	0.118
	50.2	5.39	475.72	0.443
Nickel Mine Deutz Diesel No Catalyst	30.7	26.22	223.6	0.026
	26.4	49.13	360.8	0.019

Table 12. An estimate of the percentage of PAHs in RCD samples.
Cont'd

Sample	Total PAHs ng/m^3	Wt of Extract mg	Volume m^3	% Wt of Total PAHs in extract
Nickel Mine	32.4	66.21	464.9	0.023
Deutz Diesel	32.4	66.21	411.2	0.020
PTX Catalyst				
Nickel Mine	27.4	34.85	444.2	0.047
Deutz Diesel	26.3	19.83	400	0.017
Dieseler III	106	37.59	129.3	0.036
Catalyst	65.9	13.25	116.3	0.058
	111	29.25	117.2	0.044
	154	21.44	158.0	0.113
Salt Mine	299	13.17	19.08	0.043
Caterpillar	420	14.48	12.58	0.036
Diesel				
PTX Catalyst				
Uranium Mine	496	33.38	16.1	0.024
Detroit Diesel	212	64.88	17.5	0.006
No Catalyst				

Average 0.069 ± 0.08%

the PAHs in the mine air undoubtedly arises because the PAHs account for such a small fraction of the material that is collected on filters in dieselized underground mines.

Table 13 gives the actual data obtained in the analyses of the RCD samples collected in fifteen different environments in four different nickel mines. The data includes the amount of respirable dust, the RCD in mg. and in mg/m^3, the amount of carbon on the filter, the amount of sulfate ion found in the aqueous extract from the filters both before and after they have been heated in the RCD experiment and the percentage of the sulfate ion present as sulfuric acid, in each of the mining environments. The last values were calculated from the results of the pH and the sulfate ion analyses that were carried out on the aqueous extracts from the silver membrane filters. Obviously, all of these analyses could not be carried out on the same filters. It is believed that the results can be compared however, because the filters used in each set of analyses were collected at the same time and within a few inches of one another in a drift or stope of a nickel mine. The results in Table 13 for the fifteen different mining environments where respirable dust samples were collected on silver membrane filters, were averaged. These averages are presented in Table 14.

The amount of water on four different RCD filters was determined with a Karl Fischer titration (15). The results in column 4 of Table 13 show that three out of the four samples did not contain any water and it seems probable that there is little or no water on the respirable dust filters or in the RCD.

The results in columns 5 and 6 of Table 13 show that the respirable combustible dust only accounts for an average of 0.30/0.55 or 55% of the total respirable dust in Sudbury nickel mines. This is interesting because it indicates that there is a significant amount of respirable mine dust in the air of even very humid mines. In fact, these particles of ore may be instrumental in reducing the sulfuric acid concentration in the mine air (vide supra).

The results in column 7 of Table 13 show that the RCD in the local nickel mines varies from a high of 0.92 to a low of 0.00 mg/m^3 with an average value of 0.60 ± 0.19 mg/m^3. Although the TLV has not been set for an RCD, an RCD of 2 mg/m^3 is commonly used as a standard for evaluating underground environments. The average value of 0.60 mg/m^3 and the maximun value of 0.92 mg/m^3 indicates that the RCD is well under control in the nickel mines in the Sudbury area.

The results in column 8 show that a significant portion of the RCD is carbon. In fact, carbon accounts for approximately 21% of the total RCD weight. This amount of carbon would

Table 13 The composition of RCD samples collected in nickel mines where Deutz diesels were mucking ore.

Function Sampled Location	Exhaust Treatment Device	Ventilation cfm/brake horsepower	H_2O µg	Total Particulate wgt on RCD filter mg	RCD mg	RCD mg/m^3	Carbon mg	Sulfate Ion in mg Before RCD	Sulfate Ion in mg After RCD	pH	Percent H^+ found / H^+ expected from sulfate ion conc.
Mucking, Hauling Stope A	PTX Catalyst	169	-	-	0.07 0.41 0.08	0.20 0.91 0.29	-	0.124 0.055 0.065	0.07 0.18	5.23 5.16 5.16	3.4 9.1 7.7
LHD cycle Stope D	PTX Catalyst	256	-	-	0.33 0.34	1.02 1.05	-	0.10,0.10 0.10,0.10 0.01,0.05 0.03	-	-	-
LHD cycle Drift A	PTX Catalyst	156	-	0.09,0.16 0.19,0.20 0.16,0.19 0.18,0.19 0.22,0.21 0.22	0.06 0.05 0.21 0.27	0.20 0.69 0.16 0.89	-	0.17 0.11 0.00	0.10 0.06	5.83 5.93 6.00	0.00 0.00 0.00
LHD cycle Drift B	PTX Catalyst	207	-	1.48,1.55 0.62,0.00 0.24,0.05 0.57,0.48 0.16	0.03 0.21 0.04 0.28 0.16 2.37 0.19 0.24	0.10 4.6 0.98 0.59 0.09 0.42 0.67	-	0.00 0.00	0.00,0.07 0.00,0.03 0.00,0.01 0.01,0.07	4.88 6.02 6.23 6.31	-
Hauling Dumping Drift C	PTX Catalyst	148	-	0.37,0.58 0.79,0.53 1.00,0.53 0.62,1.14 0.92,0.56 0.66,0.75	0.10 0.33	0.37 1.22	-	0.10,0.24 0.13,0.26 0.07	0.18 0.36	6.37	0.00
LHD cycle Stope E	Johnson-Mathey Catalyst	110	-	1.00 0.62	0.15 0.18 0.64 0.67 0.46	0.19 0.16 0.63 0.68 0.56	0.015 0.115 0.036	0.21,0.14 0.41,0.29 0.33,0.11 0.13	0.24 >0.30	4.83,5.35 5.21,5.43 5.47,5.42 5.27,5.46	8.0,2.1, 0.59,1.2, 2.3,0.92, 2.6,1.9
LHD cycle Stope	PTX Catalyst plus USBM filter	205	-	-	-		-	0.85,0.62 1.25,0.35 0.40,0.58 0.75,0.65 0.85,0.80	-	5.27,6.27 4.96,5.86 5.69,5.89 5.57,6.38 6.16	0.26,2.02 0.46,2.6 0.34,0.10 0.03,0.04 0.03,0.38

Table 13. The composition of RCD samples collected in nickel mines where Deutz diesels were mucking ore. Cont'd

Function Sampled Location	Exhaust Treatment Device	Ventilation cfm/brake horsepower	H_2O µg	Total Particulate wgt on RCD filter mg	RCD mg	RCD mg/m³	Carbon mg	Sulfate Ion in mg Before RCD	Sulfate Ion in mg After RCD	pH	Percent H^+ found / H^+ expected from sulfate ion conc.
LHD cycle Stope E	Johnson-Mathey Catalyst & Fume Diluter	110	-	0.17 1.58 3.06	0.69 0.74	0.85 0.92	0.151 0.178	0.13 0.22 0.24	>0.2 >0.2	5.08 5.09 4.97	2.7 2.4 6.1
Mucking Hauling Stope F	Corning Diesel Exhaust Filter	169	-	0.15 0.39 0.44 0.26 0.09	0.08 0.00 0.13 0.08	0.18 0.00 0.28 0.29	0.006 0.013	0.09,0.00 0.012 0.018	0.13 0.07	5.28,5.29 5.24 5.46	4.6 21* 20*
LHD cycle Stope E	Fume Diluter	110	-	-	0.41 0.76 0.20 0.16	0.48 0.26 0.57 0.16	-	0.121 0.148	0.11 0.20	5.08 5.22	5.0 2.9
LHD cycle Stope E	none	110	-	0.34 0.46	0.16 0.21 0.04 0.23 0.26	0.58 0.11 0.78 0.89 0.70	0.071 0.128 0.117	0.013,0.00 0.050,0.035 0.00,0.023	0.19 0.08	6.38,4.68 4.69,5.46 5.72,5.30	2.3*,7.1* 15.7*,29*
Mucking Hauling Stope F	none	169	-	0.39 0.84	0.34 0.08	0.60 0.11	-	0.00 0.065	0.20 0.10	5.11 5.24	6.4
LHD cycle Drift D, Fuel A	none	156	146 0	-	0.22 0.22	0.37 0.44	0.029 0.032 0.00	0.06 0.00	0.06 0.04	-	-
LHD cycle Drift D Fuel B	none	156	0	-	0.25	0.635	0.018	0.11	0.02	-	-
LHD cycle Drift D Fuel C	none	156	0	-	0.16	0.37	0.043	0.14 0.01	0.02	-	-
Averages				0.55± 0.54	0.30± 0.37	0.60± 0.19	0.063± 0.06	0.20± 0.27	0.11± 0.09		2.5± 2.6

* Not used in calculating the average. These values were not used because the sulfate ion concentrations that were used to calculate these values are incorrect.

Table 14. The average RCD, percent carbon, sulfate ion concentration before and after the RCD experiment and the percent sulfate ion present as sulfuric acid.

Function Sampled Location	Exhaust Treatment Device	Ventilation cfm/brake horsepower	Average Total Particulate mg	Average RCD mg	Average Carbon mg	Average Sulfate Ion Conc. Before RCD mg	Average Sulfate Ion Conc. After RCD mg	Average Percent acid / expected acid based on sulfate ion conc.	Weight % sulfate ion / RCD Before RCD	Weight % sulfate ion / RCD After RCD	Percent C / RCD by weight	Percent RCD / Total Particulate on RCD filter	Percent Sulfuric Acid / RCD
Mucking Hauling Stope A	PTX Catalyst	169	-	0.19± 0.19	-	0.08± 0.04	0.12± 0.08	6.7± 3.0	42	63	-	-	2.8
LHD cycle Stope D	PTX Catalyst	256	-	0.34± 0.01	-	0.7± 0.04	-	-	21	-	-	-	-
LHD cycle Drift A	PTX Catalyst	156	0.18± 0.04	0.15± 0.11	-	0.09± 0.09	0.08± 0.03	0.00	93	53	-	83	0.39
LHD cycle Drift B	PTX Catalyst	207	0.57± 0.58	0.44± 0.78	-	0.00± 0.00	0.02± 0.03	-	0.0	4.5	-	77	-
Hauling Dumping Drift C	PTX Catalyst	148	0.70± 0.22	0.22± 0.16	-	0.16± 0.08	0.27± 0.13	0.00	73	123	-	31	0.06
LHD cycle Stope B	PTX Catalyst + USBM Filter	205	-	-	-	0.71± 0.26	-	0.63± 0.91	-	-	-	-	-
LHD cycle Stope E	Johnson-Mathey Catalyst	110	0.81± 0.27	0.42± 0.25	0.06± 0.05	0.23± 0.11	>0.27± 0.04	2.5± 2.4	55	>55	14	52	1.3
LHD cycle Stope E	Johnson-Mathey Catalyst + Fume Diluter	110	1.60± 1.44	0.72± 0.04	0.16± 0.02	0.20± 0.06	>0.20	3.7± 2.1	28	>28	22	45	1.0
Mucking Hauling Stope F	Corning Filter	169	0.27± 0.15	0.07± 0.05	0.01± 0.005	0.03± 0.04	0.10± 0.04	15± 9.2	43	143	14	26	6.5
LHD cycle Stope E	Fume Diluter	110	-	0.38± 0.27	-	0.13± 0.02	0.16± 0.06	4.4[a] 1.5	34	42	-	-	1.4
LHD cycle Stope E	none	110	0.40± 0.08	0.18± 0.09	0.10± 0.03	0.02± 0.02	0.14± 0.08	14± 12	11	78	56	45	1.5

Table 14. Cont'd The average RCD, percent carbon, sulfate ion concentration before and after the RCD experiment and the percent sulfate ion present as sulfuric acid.

Function Sampled Location	Exhaust Treatment Device	Ventilation cfm/brake horsepower	Average Total Particulate mg	Average RCD mg	Average Carbon mg	Average Sulfate Ion Conc. Before RCD mg	Average Sulfate Ion Conc. After RCD mg	Ave. Percent [acid / expected acid based on sulfate ion]	Weight % [sulfate ion / RCD] Before RCD	Weight % [sulfate ion / RCD] After RCD	Percent [C / RCD] by weight	Percent [RCD / Total Particulate on RCD filter]	Percent [Sulfuric Acid / RCD]
Mucking Hauling Stope F	none	169	0.62± 0.32	0.21± 0.18	-	0.03± 0.04	0.15± 0.08	6.4	14	71	-	34	0.91
LHD cycle Fuel A Drift D	none	156	-	0.22	0.02± 0.02	0.03± 0.04	0.05± 0.01	-	14	23	9.1	-	-
LHD cycle Fuel B Drift D	none	156	-	0.25	0.02	0.11	0.02	-	44	8.0	7.2	-	-
LHD cycle Fuel C Drift D	none	156	-	0.16	0.04	0.08± 0.09	0.02	-	50	13	27	-	-
Averages								2.5±* 2.6	37± 26	54± 42	21.4± 16.6	49± 21	1.8± 1.9

* See column 11, Table 13.

be equivalent to approximately 25% of the RCD if all of the carbon were present as saturated and/or unsaturated (aromatic) hydrocarbons. Unfortunately, we were not able to determine whether the carbon is present as carbon particles (soot) or as saturated or unsaturated hydrocarbons.

The results in columns 9 and 10 show that significant amounts of sulfate ion are on the filters both before and after the RCD experiment. This confirms that very little of the sulfate ion is present as the volatile sulfuric acid (vide infra). Finally, the results in the last column confirm that very little of the sulfate ion is present as sulfuric acid. In fact, the best estimate (using only the results obtained where there was enough sulfate ion on the silver membrane filters) is that only 2.5% $\pm$ 2.6% of the sulfate ion in the mine air is present as sulfuric acid.

The results in Tables 12 and 14 indicate that the RCD is comprised of approximately 0.1% PAHs, 21% carbon (this would be equivalent to approximately 25% unburned hydrocarbon) and 2% sulfuric acid. Thus, we have only identified approximately 30% of the RCD. Even if all of the sulfate ion on the filter had been present as sulfuric acid and was driven off during the RCD experiment as Kirk and co-workers had assumed (5,6), we would only have identified approximately 65% of the material in the RCD sample, ie., the RCD would consist of approximately 40% sulfuric acid, 21% carbon or 25% unburned hydrocarbon and 0.1% PAHs. However, the results of the pH and sulfate ion analyses as well as the results from the RCD experiments indicate that very little of the sulfate ion is present as sulfuric acid, ie., the results in the last column of Table 13 indicate that only 2.5% $\pm$ 2.6% of the sulfate ion is present as sulfuric acid. Another piece of evidence which suggests that very little of the sulfate ion is present as sulfuric acid is presented in columns 7 and 8 of Table 14. These results show that there is more sulfate ion on the silver membrane filters after they have been heated in the RCD experiment, ie., the sulfate ion on the filters after they have been heated in the RCD experiment is an average of 54/37 or 1.46 times greater than the sulfate ion on the filters collected underground. This result is significant because it clearly demonstrates that most of the sulfate ion is not in a volatile form, ie., it must exist as inorganic (metal sulfate) salts and cannot exist as sulfuric acid. If the sulfate ion on the original filter had been present as sulfuric acid, at least some of it would have volatalized in the RCD experiment and the sulfate ion concentration on the filter would be much lower after the RCD experiment.

It is interesting to speculate on the reason the sulfate ion concentration is higher after the silver membrane filter was heated in the oven at 400 ^{o}C for an hour. One reason the sulfate ion concentration on the silver membrane filters could be higher after the RCD experiment is because heavier samples, ie., those containing more particulate, were selected for the RCD experiment. In fact, this may well be the reason that the sulfate ion concentration is higher after the filters have been treated at 400 ^{o}C. When we compared the weights of the total respirable dust on the filters used for the sulfate ion and RCD experiments, we found that the weight of respirable dust on the filters chosen for the RCD experiment was on average 46% higher than it was on the filters chosen for the sulfate ion analysis. If this was true in general, the RCD samples would contain 46% more of each substance than the samples used in the sulfate ion and pH analyses and one should correct the results obtained from the filters selected for the sulfate ion analysis by multipying the observed concentrations by 146/100. If this is done, the amount of sulfate ion on the filters before and after the RCD experiment are identical and there is no discrepancy in the amount of sulfate ion before and after the RCD experiment. Appying this correction factor is attractive because it makes the data consistent with the conclusion that almost all of the sulfate ion is present as inorganic (non-volatile) sulfate and not as sulfuric acid. Unfortunately, the comparison of the weights of the respirable dust on the filters used for the sulfate analysis and the RCD analysis could only be made on a few filters and we do not know whether correcting the sulfate ion results in this way is reasonable. Finally, it is worth noting that if this correction is valid, the percentages of all the components in the RCD should be increased by 146/100, ie., the RCD would be comprised of approximately 0.1% PAHs, 30% carbon (35% unburned hydrocarbon) and 3% sulfuric acid. It is interesting that this amount of sulfuric acid agrees very well with the 3.9% sulfuric acid that was predicted from the pH and sulfate ion analyses (see the last column of Table 13).

Another way that the sulfate ion could have increased in the RCD experiment is if some of the sulfides in the respirable mine dust (ore) on the silver membrane filter were oxidized to sulfates during the RCD experiment. This is at least possible because the respirable combustible dust only accounts for 55% of the respirable dust on the silver membrane filter. If some of the sulfide ore were oxidized to metallic sulfates in the RCD experiment, the sulfate ion concentration would be higher on the silver membrane filter after the RCD experiment because the filter would contain all of the non-volatile inorganic sulfates that were originally on the filter as well as those made by oxidizing the ore. If this occurred, the RCD would no longer reflect the amount of respirable combustable dust on the filter. Converting a significant amount

of the metal sulfides in the mine ore into the heavier sulfate salts in the RCD experiment, would increase the weight of the filter and reduce the magnitude of the RCD, ie., it would reduce the observed weight loss in the RCD experiment. This means that the the RCD experiment would underestimate the amount of respirable combustible dust (the RCD) in the mine air. In fact, it would be impossible to interprete an RCD unless one did a complete analysis of the sample both before and after the RCD experiment. In practice, this would make the RCD almost useless as a tool for monitoring the environment in a dieselized underground mine. Although the first suggestion, ie., applying a correction factor of 146/100, is more attractive because it leads to an exact sulfate ion balance in the before and after RCD samples and gives better agreement between the RCD and the pH and sulfate ion methods of estimating the percentage of sulfuric acid in the mine air, we do not have enough data to know whether either of these suggestions is correct. We can only say with certainty that most of the sulfate ion was present as sulfate ion rather than as sulfuric acid when the analyses were done.

The Effect of Catalytic Purifiers, Filters and Fume Diluters on the RCD

Table 15 examines the effect of two types of catalytic purifiers, a fume diluter and a Corning diesel exhaust filter on the composition of the RCD. The data demonstrates that the exhaust treatment device can cause significant changes in the composition of the RCD.

The Effect of Adding a Catalytic Purifier:- Two types of catalytic purifiers, a PTX and a new Johnson-Mathey catalyst were tested on Deutz F8L-714 and a Deutz A6L-714 diesel, respectively.The results for each diesel were similar. The results in column 3 show that adding the catalyst reduces the percent (carbon/RCD) from an average of 25% $\pm$ 23% for the bare engine to an average of 18% $\pm$ 4%, ie., by approximately 30%. Although the difference between the catalyzed and uncatalyzed engines is too small to be statistically significant, the effect is what one would expect. Catalytic purifiers oxidize some of the soot (carbon particles) and unburned hydrocarbon in the exhaust to carbon dioxide. This would reduce the amount of carbon-based material that would be collected on the filter and reduce the percent (carbon/RCD).

The percentage of (sulfate ion/RCD), column 4, is larger when a catalyst is used, ie., the percent of sulfate ion in the RCD is 27% $\pm$ 19% when no catalyst is used and 45% $\pm$ 32% when catalysts are used. Thus, the percent (sulfate ion/RCD) is 65% higher when a catalytic purifier is installed in the exhaust train of a Deutz diesel. This result was also expected. It

Table 15. The average composition of the RCD samples collected in stopes where Deutz diesels fitted with different exhaust treatment devices were mucking ore.[a]

Exhaust Treatment Device	Percent RCD / Total Particulate	Percent Carbon / RCD	Percent Sulfate Ion / RCD		Percent Sulfuric Acid / RCD	Percent Sulfuric acid found / Sulfuric acid expected if all the sulfate ion were sulfuric acid
			Before RCD	After RCD		
PTX Catalyst	64±28	-	46±37	55±39	1.1±1.5	2.9±4.0
Johnson Mathey Catalyst	49±4	18±4	42±19	>42±19	1.2±0.2	2.5±2.3
Corning Diesel Exhaust Filter	26	14	43	143	6.5	4.6
Fume Diluter	-	-	34	42	1.4	4.0±1.5
None	40±6	25±23	27±19	39±33	1.2±0.4	6.4
Total Catalysts	58±8	18±4	45±32	>51±32	1.1±1.1	2.7±3.1
Total No Catalyst	35±10	23±20	30±17	48±36	2.6±2.6	4.7±I.4

a. The error limits are the standard deviation. Values of greater than 100% were set equal to 100% in calculating the average values.

simply confirms the results found in the sulfate ion analyses, ie., that adding a catalyst increases the sulfate ion in the exhaust significantly.

The percent (RCD/Total respirible dust), column 2, is higher when a catalyst is used, ie., the RCD represents an average of 40% $\pm$ 6% of the total respirable dust when no exhaust treatment device is used whereas the average percent (RCD/Total respirable dust) is approximately 45% higher, ie., an average of 58% $\pm$ 8% when a catalyst is used. This result seems unreasonable at first glance because the catalyst reduces the amount of carbon in the RCD. However, adding the catalyst almost doubles the amount of sulfate ion and sulfuric acid in the exhaust. This increase in the volatile sulfuric acid would increase the magnitude of the RCD and the percent (RCD/Total respirable dust).

The average percent (sulfate ion/RCD) on the filters analyzed after the RCD experiment (column 5) for diesels working with and without catalytic purifiers in the exhaust system are >51% $\pm$ 32% and 39% $\pm$ 33%, respectively. This more than 30% increase in sulfate ion on adding the catalyst compares reasonably well with the 65% increase in sulfate ion found in the before the RCD sulfate ion analyses. These results also confirm that adding a catalyst increases the amount of sulfate ion in the exhaust.

One unexpected result, column 6, was that the catalyst did not affect the percent sulfuric acid in the RCD, ie., the average percent (sulfuric acid/RCD) was 1.1% $\pm$ 1.5% when a catalyst was used and 1.2% $\pm$ 0.4% when no catalyst was in the exhaust system. This was a surprise because adding a catalyst almost doubles the amount of sulfate ion in the exhaust but does not change the (sulfuric acid/sulfate ion) ratio. Thus, we would have expected the percent (sulfuric acid/RCD) to be between 50% and 100% higher when catalysts were used. We cannot explain this result.

Finally, the results in the last column of Table 15 show that the percent (sulfuric acid found/sulfuric acid expected if all of the sulfate ion were present as sulfuric acid) is within experimental error the same, ie., 2.7% $\pm$ 3.1% when a catalyst is used and 4.7% $\pm$ 1.4% when the diesel was operated without a catalytic purifier. Unfortunately, we were not able to collect enough good samples to obtain an acceptable base line measurement of the sulfate ion in the exhaust from a bare engine (vide supra). As a result, we cannot be certain how the catalyst affects the amount of sulfuric acid in the exhaust. However, it appears that adding the catalyst does not affect the percent (sulfuric acid/sulfate ion) significantly. More definitive results await more tests. We cannot explain why the average percentage of (sulfuric acid/sulfate ion) is not affected by a catalyst. In fact, we expected higher percentages of sulfuric acid

in the exhaust when engines operated with a catalyst because catalytic purifiers oxidize more of the fuel-generated sulfur compounds to sulfuric acid (vide supra).

The Effect of Adding a Corning Diesel Exhaust Filter:- One would expect that the percent (RCD/Total respirable dust) and the percent carbon in the RCD would be lower when a Corning filter is used because the Corning filter removes a large amount of the soot (carbon particles and the adsorbed hydrocarbons) from the exhaust (16). Indeed, smaller percentages of (RCD/Total respirable dust) and (carbon/RCD) are found with engines fitted with a Corning filter. The results in column 2 show that the the RCD only represents 26% of the total respirable particulate weight when a Corning filter is used whereas the RCD represents an average of 40% $\pm$ 6% of the Total respirable dust when no exhaust treatment device is used. Thus, the Corning filter reduces the percentage (RCD/Total respirable dust) by 35%. The results in column 3 show that the percent (carbon/RCD) decreases from 25% $\pm$ 23% when no catalyst is used to 14% when a Corning filter is in the exhaust system of the diesel. Although the differences in the percent (carbon/RCD) for the engines operating with and without the Corning filter, are too small to be statistically different at a high confidence level, the percentage carbon is 45% lower when a Corning filter is used and it appears that the Corning filter does reduce the amount of carbon in the RCD.

Some unexpected results were obtained when the Corning filter was used. One of the surprising results was the unreasonably high percentage of (sulfate ion/RCD) on the filters analyzed after the RCD experiment (column 5). Unfortunately, only two samples could be collected when the Corning filter was being tested and we do not know whether this result is correct.

The second surprising result for the Corning filter was that the percentage of sulfate ion in the RCD was 60% higher when the Corning filter was on the diesel. This was completely unexpected because the Corning filter was not thought to oxidize the sulfur dioxide in the exhaust. The Corning filter is again unusual when one examines the percent (sulfuric acid/RCD) results in column 6. The percent sulfuric acid is approximately 5 times higher in the RCD samples collected downstream from the diesel fitted with the Corning filter. We are unable to suggest a reason for these completely unexpected results. However, an examination of the results in Table 13 shows that the RCDs were very small when the Corning filter samples were collected and it is possible that these unexpected results arise from an error in measuring these RCDs. In fact, the results in the following paragraph show that the amount of sulfuric acid does not increase when the Corning filter is added to the diesel. This supports our

hypothesis that the percent (sulfate ion/RCD) and the percent (sulfuric acid/RCD) may not increase when the Corning filter is used and that there is an error in the RCD values for the Corning filter.

Finally, the results in the last column of Table 15 suggest that the percent (sulfuric acid found/sulfuric acid expected if all of the sulfate ion were present as sulfuric acid) is not affected significantly by the Corning filter, ie., the ratio is approximately 30% lower (4.6% versus 6.4%) when the diesel is operating with the Corning filter in the exhaust system. We did not expect a significant effect in the percent (sulfuric acid found/sulfuric acid expected) because the Corning filter does not oxidize sulfur dioxide to sulfuric acid.

The Effect of Adding a Fume Diluter;- Adding a fume diluter to the exhaust train of a Deutz diesel increases the percent (sulfate ion/RCD) by approximately 26%. This presumably occurs because a small amount of sulfur dioxide is oxidized to sulfuric acid when mine air is drawn into the fume diluter to dilute the exhaust. The increase in the percentage of (sulfate ion/RCD) from 34% before heating to 42% after heating the silver membrane filter in the RCD experiment, means that the percentage of (sulfate ion on the filter after it had been heated in the RCD experiment/RCD) is approximately 25% higher than that found before the RCD experiment.While the results confirm that most if not all, of the sulfate ion on the filters is in the form of sulfate ion, we do not know whether the increase in the amount of sulfate ion is significant because only two samples were analyzed.

The percent (sulfuric acid/RCD), column 6, found when the diesel was working with and without the fume diluter are identical within the experimental error of the method, ie., the percent sulfuric acid is 1.4% when the fume diluter is used and 1.2% $\pm$ 0.4% when no exhaust treatment device is on the diesel. This was expected because the the non-oxidizing fume diluter and the bare engine should both oxidize the same amount of sulfur dioxide to sulfuric acid.

Finally, the fume diluter appears to reduce the percent of (sulfuric acid expected/sulfuric acid expected if all of the sulfate ion had been present as sulfuric acid) from the 6.4% found with the bare engine to 4.0%, ie., by approximately 40%. Unfortunately, this conclusion is only based on two samples and is therefore, not proven. While adding the fume diluter appears to reduce the percent sulfuric acid in the exhaust slightly, the important result from an industrial health point of view, is that the fume diluter certainly does not increase the amount of sulfuric acid in the exhaust significantly.

The Effect of Increasing the Sulfur Content of the Fuel

Table 16 gives the results found when three different fuels; a low sulfur, low aromatic (Jet-A1) fuel, a No. 1 diesel fuel and a high sulfur, high aromatic 1990 type fuel, were burned in a Deutz diesel with no exhaust treatment device. Although the number of samples was too few to give definitive results, there does seem to be three trends in the percent composition of the RCD. The first trend is that the RCD increases as a more aromatic fuel is burned in the diesel. This suggests that there is more carbon (soot) and/or more unburned hydrocarbon in the exhaust when a more aromatic fuel is burned. This is in fact, what one would expect. Fuels with higher percentages of aromatics are thought to burn less completely in a diesel engine and thus one would expect more unburned hydrocarbons and more soot (more carbon) in the exhaust from an engine burning a more aromatic fuel. As a result, there would be more carbon and unburned hydrocarbon collected on the RCD filter and a higher percent RCD would be observed.

The second trend seems to be at odds with the first. Although the number of samples was small and the differences in the amount of carbon are small, the percent carbon does appear to decrease when a more aromatic fuel is burned in the diesel engine. We would have predicted the opposite trend and are therfore, not able to explain these results.

The third trend is in the percent (sulfate ion/RCD) in the RCD samples analyzed before the RCD experiment. Again, if one ignores the single very high amount of sulfate ion (0.14 mg) in the exhaust for the Jet-A1 fuel, the percent (sulfate ion/RCD) for the Jet-A1 fuel is only 6.3% and the sulfate ion increases as a percentage of the RCD when the amount of sulfur in the fuel is increased. This is what one would predict because more sulfate ion should be in the mine air when a higher sulfur fuel is used.

The data in column 6 of Table 16 indicates that the fuel does not affect the amount of water in the RCD significantly.

Finally, the fuel seems to affect the form of the sulfate ion in the exhaust. If the trend in the percent sulfate ion before the RCD is real, then there is a change in the percent (sulfate ion after the RCD/RCD) when the fuels are changed. The sulfate ion after the RCD experiment is higher than that in the original sulfate ion samples for both the Jet-A1 and the regular No. 1 diesel fuels indicating that most of this sulfate is present as sulfate salts. The sulfate ion after the RCD experiment for the high sulfur, 1990 type fuel on the other hand, is much lower than the sulfate ion before the RCD experiment. One explanation for

Table 16. The RCD, the sulfate ion, the carbon and water concentrations on RCD samples collected in a drift where a 180 horsepower F8L-714 Deutz diesel* burning three different types of fuels was mucking ore.

Fuel	Weight percent sulfur in Fuel	Percent Aromatics	Cetane Index	RCD mg	Water on filter in µg	Carbon on filter in mg	Sulfate ion in mg		Percent $\frac{C}{RCD}$	Percent $\frac{\text{Sulfate ion before RCD}}{RCD}$	Percent $\frac{\text{Sulfate Ion after RCD}}{RCD}$
							Before RCD	After RCD			
low sulfur low aromatic Jet A-1 fuel	0.007	25.0	44.9	0.16	0	0.043	0.14 0.01	0.02	27	47 (6.3)**	13
regular No. 1 diesel fuel	0.085	28.9	46.7	0.22 0.22	146 0	0.029 0.032	0.00 0.06	0.06 0.04	14	14	28
high sulfur high aromatic 1990-type fuel	0.49	33.6	37.7	0.25	0	0.018	0.11	0.02	7.2	44	8

* The ventilation averaged 29,000 cfm or 156 cfm/brake horsepower.
** Calculated for a sulfate ion concentration of 0.01 mg.

this is that the sulfate ion is mainly present as sulfuric acid when the high sulfur fuel is burned but is mainly present as sulfate ion when the normal and Jet-A1 fuels are burned. If this were the case, it would help to explain the high RCD that was found when the more aromatic, high sulfur 1990 type fuel was used, ie., if this were the case, part of the increase in the RCD weight loss would be due to loss of sulfuric acid.

CONCLUSIONS

This work has shown that the silver membrane filter is clearly the best filter for collecting sulfate ion (sulfuric acid) samples and RCD samples in dieselized underground mines. In fact, the silver membrane filter was superior from all but one point of view and it was only marginally worse than the best filter in this test, ie., it was i) neutral and caused the smallest change in the pH of the water used to extract the filters, ii) it had within experimental error, the lowest buffering capacity, iii) it was the lowest in extractable sulfate ion and iv) oxidized less sulfur dioxide than any of the other filters we tested. The cellulose filter was eliminated because it neutralized a significant amount of sulfuric acid. The PVC filter was unacceptable because it oxidized too much SO_2 to sulfuric acid. The Whatman FG/A and the Gelman Spectrograde silica filters (7) were judged unacceptable in all four tests. As a result, all sulfate ion and RCD samples should be collected on silver membrane filters.

Samples collected in various stopes and drifts show that significant amounts of ammonia can be added to the mine air during the mucking operation. In fact, (ammonia/sulfate ion) ratios as large as 1.00 have been found in underground mines and the average value of the ratio in the few stopes where ammonia was found is 0.53. If one assumes that all of the sulfate ion is present as sulfuric acid, there is sufficient ammonia to neutralize 25% of the sulfuric acid that was present in these environments. This means that it is important to determine the amount of ammonia before trying to assess the amount of sulfuric acid in the mine air. It is worth noting that all of the ammonia concentrations we found near underground mucking operations were far below the TLV for ammonia.

The pH and sulfate ion analyses on the silver membrane filters collected in seventeen environments in four different nickel mines have shown that the average sulfuric acid levels are significantly below the TLV values in the local nickel mines. In fact, the results show that the sulfate ion concentrations vary from 0.00 to 3.40 mg/m^3 and that only 10 out of 75 or 13% of the samples exceed the 1.0 mg/m^3 TWA-TLV concentration for sulfuric acid. The average sulfate ion concentration is only 0.49 $\pm$ 0.67 mg/m^3 or only half of the TLV concentration. Of even more importance however, is the observation that only a very small proportion, ie., 3.8% $\pm$ 2.6% of the sulfate ion is present as sulfuric acid and that only 2.6% $\pm$ 1.5% of the sulfur compounds in the fuel are present as sulfuric acid on the silver membrane filters. This latter value is extremely close to the 2.4% of the sulfur compounds in the diesel fuel that were converted into sulfuric acid by diesel trucks in the tunnels on the Pennsylvania

Turnpike. The very close agreement between the results of these two studies suggests that the percentage of sulfuric acid found in the mine environment is correct.

The results also show that the sulfuric acid (sulfate ion) drops out of the mine air very rapidly in nickel mines. In fact, the percent recovery of the sulfur compounds in the fuel is only 47% in a fairly dry nickel mine and 13% in a humid nickel mine. It is postulated that the sulfuric acid and/or sulfate salts dissolve in water droplets in a humid mine to form heavy droplets of a dilute sulfuric acid solution which fall rapidly to the floor of the drift. In a drier mine, the sulfuric acid (sulfate ion) travels for longer, but still fairly short distances, ie., only half of the fuel-generated sulfur compounds are found when samples are collected between 10 and 150 feet downstream from the diesel in a fairly dry mine. In a very dry mine, eg., a salt mine, the behaviour is unknown. It would be interesting to analyze a few samples from a dry mine to study how the sulfuric acid behaves in this environment.

All of these factors combine to suggest that very little of the sulfuric acid formed in the engine or exhaust system of a diesel is in the form of sulfuric acid at the sampling site in underground nickel mines. If the sulfuric acid is converted into sulfate ion in the catalytic purifier or in a fast reaction with the respirable-sized ore particles rather than slowly on the silver membrane filter, it is highly unlikely that a miner would ever be exposed to concentrations of sulfuric acid mist that would even approach the TLV level in one of the local nickel mines. Although the conclusion is much less certain for miners in other mines, the results suggest that sulfuric acid mists would not cause a health hazard in any underground mine.

As expected, adding a catalytic purifier to the exhaust train of a Deutz diesel increases the amount of sulfate ion in the exhaust by between 73% and 115% with the average increase being 90% $\pm$ 22%. This agrees very well with the results obtained in laboratory studies by Lawson et. al. who found that adding a catalytic purifier to a Deutz diesel increased the sulfate ion concentration by 50%. Catalysts also increase the percent (sulfate ion/total fuel-generated sulfur compounds) in the mine air significantly. One surprising finding is that the percentage of (sulfuric acid/sulfuric acid expected if all of the sulfate ion were present as sulfuric acid) in the mine air is not altered significantly by a catalyst. However, adding the catalyst still increases the amount of sulfuric acid in the mine air because the catalyst increases (almost doubles) the sulfate ion in the exhaust.

Although adding a fume diluter appears to reduce the sulfate ion concentration in the mine air by approximately 20%, it has little or no affect on the percent (sulfate ion/Total sulfate ion), the percent (sulfuric acid/sulfate ion) or the percent (sulfuric acid/sulfuric acid expected if all of the sulfate ion was present as sulfuric acid). This is expected because the fume diluter is not designed to oxidize sulfur dioxide to sulfur trioxide (sulfuric acid).

Although the results obtained for the Corning filter have not been proven because we were not able to collect enough samples, it appears that the Corning filter is unusual. Adding a Corning diesel exhaust filter to a Deutz diesel reduces the amount of sulfate ion in the exhaust by 30%. This was not expected because the Corning filter was designed to remove the particulate material but not the sulfuric acid and/or sulfate ion from the exhaust. The only rationale for the reduction in sulfate ion is that a significant amount of the sulfate ion (sulfuric acid) is absorbed on the particulate that is captured by the filter. Finally, the Corning filter does not seem to alter the percentage (sulfuric acid/sulfuric acid expected if all of the sulfate ion were present as sulfuric acid) in the exhaust. This was expected because the Corning filter is not an oxidizing type of exhaust treatment device.

In conclusion, the amount of sulfuric acid collected on the silver membrane filters in seventeen different mining environments is not affected significantly (from a health point of view) by any of the exhaust treatment devices that we tested, ie., it appears that adding a catalyst does not increase the amount of sulfuric acid enough to make one concerned about a miner's exposure to sulfuric acid mists in underground mines.

Finally, the results suggest that the sulfate ion (sulfuric acid) concentrations in the mine air increase as the percentage of sulfur in the fuel increases. Thus, the current practice of using a low sulfur fuel in underground mines should be continued until we can collect sufficient samples to establish whether the sulfuric acid concentration in the mine air is related to the percent sulfur in the fuel.

The RCD values found in fifteen different mining environments in four different nickel mines range from a low of zero to a high of 0.92 mg/m^3 with the average value being 0.60 $\pm$ 0.19 mg/m^3. Since a value of 2 mg/m^3 is commonly used to assess mining environments, the RCD level in the local nickel mines is well under the loosely accepted standard and the particulate levels (the RCD) in these mines should not be of concern from an industrial health point of view.

These results also show that the respirable combustible dust is accompanied by a significant amount of mine dust (ore). In fact, 45% of the respirable dust is not volatile or combustible and is not lost in the RCD experiment. This was surprising because the nickel mines we sampled were humid and it appeared that there was very little mine dust in the air. This dust may provide a mechanism for converting some of the sulfuric acid into sulfate ions.

The analyses performed on the respirable dust samples collected in fifteen environments in four different nickel mines have shown that there is little or no water in the RCD samples and that the RCD is composed of approximately 0.1% PAHs, 21% carbon or 25% unburned hydrocarbon and 2% sulfuric acid. This means that we have only been able to identify approximately 30% of the RCD material.

The sulfate ion analysis of the silver membrane filters both before and after the filters were heated in the RCD experiment, showed that there was 1.46 times more sulfate ion on the filters after the RCD experiment. Although the higher percentage of sulfate ion on the filter after the RCD experiment, may have been the result of selecting heavier (containing more particulate) filters for the RCD analysis and lighter filters for the sulfate ion analysis, the results force one to conclude that almost all of the sulfate ion on the silver membrane filters collected underground is present as non-volatile metal sulfate salts and not as the volatile sulfuric acid.

Adding a catalytic purifier to the exhaust system of a Deutz diesel increases the percent (RCD/Total Respirable Dust) by 45%, reduces the percent (carbon/RCD) by 30%, increases the percent (sulfate ion before the RCD/RCD) by 65% and the percent (sulfate ion found after the RCD/RCD) by at least 30%. The decrease in the amount of carbon occurs because the catalyst oxidizes some of the soot and/or unburned hydrocarbons in the exhaust to carbon dioxide. The increase in the amount of sulfate ion was obviously found because platinum-based catalysts oxidize the sulfur dioxide to sulfuric acid. The increased (RCD/Total respirable dust) may be due to the extra sulfuric acid that is on the filters when the catalyst is used. It is worth noting that the 65% and the >30% increases in the percent (sulfate ion/RCD) that are found before and after the RCD experiment are in reasonable agreement. The one surprising result is that adding the catalyst does not alter the percentage of (sulfuric acid/RCD) or the percent (sulfuric acid/sulfuric acid expected if all of the fuel sulfur was converted into sulfuric acid) significantly even though the catalyst oxidizes more sulfur dioxode to sulfuric acid. We do not understand why this result was found.

Adding a fume diluter increases the precent (sulfate ion/RCD) by 26% but does not affect the percentage of the (sulfate ion after the RCD/RCD), the percent (sulfuric acid/RCD) or the percent (sulfuric acid/sulfuric acid expected if all of the sulfate ion were present as sulfuric acid). While the last three effects were expected for this non-oxidizing type of exhaust treatment device, the former result was not. The 26% increase in the amount of sulfate ion may have arisen because the air that is pulled in by the fume diluter oxidizes some of the sulfur dioxide to sulfuric acid.

While the Corning diesel exhaust filter affects some of the components in the RCD as one would expect, there are also some unexpected results. The 45% decrease in the percent (carbon/RCD) and the 35% reduction in the percent (RCD/Total respirable dust) that are observed when the Corning filter is used, were expected because the Corning filter removes the soot and some of the unburned (absorbed) hydrocarbon from the exhaust. This means that both the amount of carbon and the RCD would be lower when a Corning filter is installed on the diesel. The surprising results were that the Corning filter increased the percent (sulfate ion/RCD) by 60% and the percent (sulfuric acid/RCD) by 500%. It is difficult to understand how these increases would arise in this non-oxidizing type of filter. Finally, the percent (sulfuric acid/ sulfuric acid expected if all of the sulfate ion were present as sulfuric acid) does not seem to change when a Corning filter is added to the diesel. This result which was expected, suggests that the amount of sulfuric acid did not change when the Corning filter was added. This makes it seem likely that the 60% increase in the percent (sulfate ion/RCD) and the 500% increase in the percent (sulfuric acid/RCD) are due to errors in determining the amount of respirable combustible dust (the RCD) that was collected when the Corning filter was on the diesel.

Changing from a low aromatic, low sulfur (Jet-A1) fuel to a high sulfur, high aromatic 1990-type fuel leads to a higher percentage (RCD/Total respirable dust). In addition, there is an increase in the amount of sulfate ion and sulfuric acid in the exhaust. These results can be rationalized because a more aromatic fuel burns less efficiently. This means that the amount of unburned hydrocarbon and soot (carbon particles), ie., the percent carbon, should be higher in the exhaust when a more aromatic fuel is burned. The percent (RCD/Total respirable dust) would also increase if the the amount of sulfuric acid in the exhaust was increased when the sulfur content of the fuel was increased, ie., the amount of material lost in the RCD experiment would increase because there would be more of the volatile sulfuric acid on the filters collected downstream from a diesel burning a high sulfur fuel. Finally, changing to a more aromatic, high sulfur fuel decreases the percent (carbon/RCD). We are unable to explain

this finding which appears to contradict the increase that is observed in the percent (RCD/ Total respirable dust).

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POOR

QUALITY

ORIGINAL